TECHNICAL METHODS OF CHEMICAL ANALYSIS

LUNGE AND KEANE'S

TECHNICAL METHODS OF CHEMICAL ANALYSIS

SECOND EDITION

EDITED BY

CHARLES A. KEANE, D.Sc., Ph.D.

FORMERLY PRINCIPAL OF THE SIR JOHN CASS TECHNICAL INSTITUTE, LONDON

AND

P. C. L. THORNE, M.A., M.Sc., Ph.D.

CHIEF LECTURER IN CHEMISTRY, WOOLWICH POLYTECHNIC

VOLUME II

GURNEY AND JACKSON

LONDON: 33 PATERNOSTER ROW, E.C. 4

EDINBURGH: TWEEDDALE COURT

1928

PREFACE

As in Volume I. of the present edition of *Technical Methods of Chemical Analysis*, all the sections have been thoroughly revised and brought up to date and the latest English and American methods incorporated.

The arrangement of the contents has been modified by grouping correlated industries together, so as to make the volume very largely self-contained. From this standpoint a separate section has been allotted to Metallic Salts, in which subjects which were previously distributed in other sections have been grouped together, with the addition of much new matter, and the new section on Paint Vehicles, Japans and Varnishes which has been added as a sequel to the section on Paints and Pigments, includes the relevant subject-matter of the section on Resins, Balsams, and Gum Resins of the first edition.

Numerical data have been calculated from the atomic weights published by the International Union in 1925, with such approximations as are usual, though empirical factors are retained where they are commonly used in technical work. Temperatures are stated in degrees Centigrade unless other scales are specially indicated.

The Editors desire to record their thanks to Messrs Baird and Tatlock (London), Messrs Gallenkamp, Messrs Griffin & Co., The Institute of Metals, The Institution of Mining and Metallurgy, The Arthur H. Thomas Co., The Iron and Steel Institute, and the British Engineering Standards Association for the loan of blocks or drawings, or for permission to reproduce illustrations; and to the latter Association and to the General Medical Council for permission to quote from their official publications as indicated in the text.

CHARLES A. KEANE.
P. C. L. THORNE.

CHILHAM, CANTERBURY;
WOOLWICH, S.E. 18.

April, 1928.

CONTRIBUTORS TO VOLUME II.

Iron and Steel.

By C. O. BANNISTER, M.Eng., A.R.S.M., F.I.C., Professor of Metallurgy in the University of Liverpool.

Non-Ferrous Metals.

By C. O. BANNISTER, M.Eng., A.R.S.M., F.I.C., and GEORGE PATCHIN, A.R.S.M., M.I.M.M., Principal and Head of the Metallurgy Department, Sir John Cass Technical Institute, London.

Metallic Salts.

By W. R. SCHOELLER, Ph.D., Metallurgical Chemist, London.

Potassium Salts.

By J. T. DUNN, D.Sc., F.I.C , Consulting Chemist, Newcastle-on-Tyne.

Paints and Pigments.

By R. S. MORRELL, M.A., Ph.D., F.I.C., and W. E. WORNUM, B.Sc., A.R.C.S., Messrs Mander Bros., Ltd., Wolverhampton.

Paint Vehicles, Japans and Varnishes.

By R. S. MORRELL, M.A., Ph.D., F.I.C.

ABBREVIATED TITLES OF JOURNALS

ABBREVIATIONS.	JOURNALS.
Acetylene	Acetylene
Amer. Chem. J.	American Chemical Journal
Amer. J. Sci.	American Journal of Science
Analyst	The Analyst
Annalen	Annalen der Chemie
Ann. Physik	Annalen der Physik
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie
Annali Chim. Appl.	Annali di Chimica Applicata
Ann. Chim. Phys.	Annales de Chimie et de Physik
Ann. Falsif.	Annales des Falsifications
Apoth.-Zeit.	Apotheker-Zeitung
Arch. Pharm.	Archiv der Pharmacie
A. S. T. M. Standards	Standards of the American Society for Testing Materials
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei
Berg u. Hütten. Zeit.	Berg und Hüttenmännische Zeitung
Ber.	Berichte der deutschen chemischen Gesellschaft
Ber. deutsch. Physik. Ges.	Berichte der deutschen physikalischen Gesellschaft
Biedermann's Zentr.	Biedermann's Zentralblatt für Agricultur Chemie
Boll. chim. farm.	Bollettino chimico farmaceutico
B. P.	British Patent
Brewer's J.	Brewer's Journal
Brit. and Col. Drug.	British and Colonial Druggist
Bull. Acad. Sci. Roumaine	Bulletin de la Section Scientifique de l'Académie Roumaine
Bull. Assoc. Belg. des Chim.	Bulletin de l'Association Belgique des Chimistes
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association chimique de Sucre et de Distillerie
Bull. Soc. Chim. Belg.	Bulletin de la Société chimique de Belgique
Bull. Soc. Chim.	Bulletin de la Société chimique de Paris
Bull. Soc. Ind. Nord	Bulletin de la Société Industrielle du Nord de la France
Bull. Soc. Ind. Mulhouse	Bulletin de la Société Industrielle de Mulhouse
Chem. News	Chemical News
Chem. Trade J.	Chemical Trade Journal
Chem. Zeit.	Chemiker Zeitung
Chem. Zeit. Rep.	Chemiker Zeitung Repertorium
Chem. Ind.	Chemische Industrie
Chem. Rev. Fett-Ind.	Chemische Revue über die Fett- und Harz-Industrie
Chem. Zentr.	Chemisches Zentralblatt
Chem. and Drug.	Chemist and Druggist
Chem. and Met. Eng.	Chemical and Metallurgical Engineering
Chem. Weekblad	Chemisch Weekblad
Comptes rend.	Comptes rendus hebdomadaires des séances de l'Académie des sciences

Abbreviations.	Journals.
Dingl. polyt. J.	Dingler's polytechnisches Journal
Electrician	Electrician
Electrochem. Ind.	Electrochemical and Metallurgical Industry
Electrotech. Zeitsch.	Electrotechnische Zeitschrift
Engineer	Engineer
Engineering	Engineering
Eng. and Min. J.	Engineering and Mining Journal
Farben-Zeit.	Farben-Zeitung
Färber-Zeit.	Färber-Zeitung
Fischer's Jahresber.	Fischer's Jahresbericht
Gas J.	Gas Journal
Gazz. Chim. Ital.	Gazzetta Chimica Italiana
Gerber	Der Gerber
Gerber Zeit.	Deutsche Gerber Zeitung
Ger. Pat.	German Patent
Giorn. Chim. Ind. Appl.	Giornate di Chimica Industriale ed Applicata
Gummi-Zeit.	Gummi-Zeitung
Helv. Chim. Acta	Helvetica Chimica Acta
India-rubber J.	India-rubber Journal
Ind. Bl.	Industrie Blatt
Ind. Eng. Chem.	Industrial and Engineering Chemistry
Int. Sugar J.	International Sugar Journal
Jahresber. d. chem. Techn.	Jahresbericht der chemischen Technologie
Jahresber. d. Pharm.	Jahresbericht der Pharmazie
Jahresber. f. Chem.	Jahresbericht für Chemie
J. Agric. Sci.	Journal of Agricultural Science
J. Amer. Chem. Soc.	Journal of the American Chemical Society
J. Anal. and Applied Chem.	Journal of Analytical and Applied Chemistry
J. Chem. Met. Soc., S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa
J. Chem. Soc.	Journal of the Chemical Society
J. Chem. Soc. Abstr.	Journal of the Chemical Society, Abstracts
J. Franklin Inst.	Journal of the Franklin Institute
J. Gasbeleucht.	Journal für Gasbeleuchtung und Wasserversorgung
J. Gas Lighting	Journal of Gas Lighting
J. Inst. Brewing	Journal of the Institute of Brewing
J. Inst. Mech. Eng.	Journal of the Institution of Mechanical Engineers
J. Inst. Metals	Journal of the Institute of Metals
J. Iron and Steel Inst.	Journal of the Iron and Steel Institute
J. Oil and Col. Chem. Assoc.	Journal of the Oil and Colour Chemists Association
J. Pharm. Chim.	Journal de Pharmacie et de Chimie
J. Phys. Chem.	Journal of Physical Chemistry
J. prakt. Chem.	Journal für praktische Chemie
J. Physik	Journal der Physik
J. Physique	Journal de Physique et le Radium
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia
J. Soc. Arts	Journal of the Royal Society of Arts
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry
J. Soc. Dyers and Col.	Journal of the Society of Dyers and Colourists
Kolloid Z.	Kolloid Zeitschrift
Landw. Versuchs-Stat.	Die landwirthschaftlichen Versuchs-Stationen
Leather Tr. Rev.	Leather Trades Review
Mitt. k. Materialprüf.	Mittheilungen aus dem königlichen Materialprüfungsamt zu Gross-Lichterfelde West
Mitt. techn. Gew. Museums	Mittheilungen des technischen Gewerbemuseums in Wien

ABBREVIATIONS.	JOURNALS.
Mitt. Zentralst. Wiss.-tech. Unters.	Mittheilungen aus der Zentralstelle für wissenschaftlich-technische Untersuchungen
Monatsh.	Monatshefte für Chemie der kaiserlichen Akademie der Wissenschaften, Wien
Monatsschrift f. Text.-Ind.	Monatsschrift für Textil-Industrie
Monit. Scient.	Moniteur Scientifique
Nuovo Cimento	Il Nuovo Cimento
Oesterr. Chem. Zeit.	Oesterreichische Chemiker Zeitung
Oesterr.-Ungar Zeitschr.	Oesterreichisch-Ungar Zeitschrift für Zuckerindustrie und Landwirthschaft
Oesterr. Zeitsch.	Oesterreichische Zeitschrift für Berg- und Hüttenwesen
Paper and Pulp	Paper and Pulp
Papier-Zeit.	Papier-Zeitung
Petrol. Rev.	Petroleum Review
Pharm. J.	Pharmaceutical Journal
Pharm. Rev.	Pharmaceutical Review
Pharm. Weekblad	Pharmazeutisch Weekblad
Pharm. Zeit.	Pharmazeutische Zeitung
Pharm. Zentralh.	Pharmazeutische Zentralhalle
Pharm. Zentr.	Pharmazeutisches Zentralblatt
Phil. Mag.	Philosophical Magazine and Journal of Science
Phil. Trans.	Philosophical Transactions of the Royal Society
Phys. Rev.	Physical Review
Proc. Amer. Acad.	Proceedings of the American Academy
Proc. Amer. Electrochem. Soc.	Proceedings of the American Electrochemical Society
Proc. Amer. Inst. Min. Eng.; Bull. Amer. Inst. Min. Eng.	Proceedings and Bulletin of the American Institute of Mining Engineers
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society
Proc. Amer. Soc. Test. Mats.	Proceedings of the American Society for Testing Materials
Proc. Inst. Civ. Eng.	Proceedings of the Institution of Civil Engineers
Proc. Inst. Mech. Eng.	Proceedings of the Institution of Mechanical Engineers
Proc. Inst. Min. and Met.	Proceedings of the Institution of Mining and Metallurgy
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam, Proceedings (English Edition)
Proc. Phys. Soc.	Proceedings of the Physical Society of London
Rev. Gen. Mat. Col.	Revue Générale des Matières Colorantes
Rev. intern. Falsif.	Revue internationale des Falsifications
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique
Roy. Soc. Proc.	Proceedings of the Royal Society
Scient. Amer.	Scientific American
Stahl u. Eisen	Stahl und Eisen
Staz. speriment. agr. Ital.	Le Stazione sperimentali agrarie Italiane
Tonindustrie Zeit.	Tonindustrie Zeitung
Trans. Amer. Inst. Min. Eng.	Transactions of the American Institute of Mining Engineers
Trans. Faraday Soc.	Transactions of the Faraday Society
Trans. Inst. Min. and Met.	Transactions of the Institution of Mining and Metallurgy
U.S. Cons. Reps.	United States Consular Reports
West Ind. Bull.	West Indian Bulletin
Woch. f. Brau.	Wochenschrift für Brauerei
Z. anal. Chem.	Zeitschrift der analytischen Chemie
Z. angew. Chem.	Zeitschrift für angewandte Chemie
Z. anorg. Chem.	Zeitschrift der anorganische Chemie

ABBREVIATIONS.	JOURNALS.
Z. Elektrochem.	Zeitschrift für Elektrochemie
Z. Farb. Ind.	Zeitschrift für Farben Industrie
Z. Farb.- u. Text.-Chem. . .	Zeitschrift für Farben- und Textil-Chemie
Zeitschr. f. landw. Versuchswesen, Österr.	Zeitschrift für das landwirtschaftliche Versuchswesen in Österreich
Z. für chem. Apparatenkunde .	Zeitschrift für chemische Apparatenkunde
Z. ges. Brauw.	Zeitschrift für das gesammte Brauwesen
Z. ges. Schiess- u. Sprengstoffw. .	Zeitschrift für das gesamte Schiess- und Sprengstoffwesen
Z. Instrumentenk. . . .	Zeitschrift für Instrumentenkunde
Z. öffentl. Chem. . . .	Zeitschrift für öffentliche Chemie
Z. physik. Chem. . . .	Zeitschrift für physikalische Chemie
Z. Spiritusind.	Zeitschrift für Spiritusindustrie
Z. Unters. Nahr. u. Genussm. .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel
Z. Ver. deut. Zuckerind. . .	Zeitschrift des Vereins der deutschen Zucker-Industrie
Z. Verein. deutsch. Ingen. . .	Zeitschrift des Vereins deutscher Ingenieure
Z. Zuckerind. Böhm. . . .	Zeitschrift für Zuckerindustrie in Böhmen

CONTENTS OF VOLUME II.

Paints and Pigments.

TECHNICAL METHODS OF CHEMICAL ANALYSIS

IRON AND STEEL

By C. O. BANNISTER, M. Eng., A.R.S.M., F.I.C., Professor of Metallurgy, University of Liverpool.

THE manufacture of iron and steel may be divided into two main branches—viz., the preparation of pig iron by blast furnace smelting, and its conversion into malleable iron or steel by various processes.

The raw materials of the former process are iron and manganese ores, fluxes, and fuels, whilst the main products are iron, slag, and furnace gases. In the processes used for the manufacture of malleable iron and steel, pig iron, scrap, fluxes, ferromanganese, ferrosilicon, etc., are the raw materials used, whilst the products are the numerous varieties of malleable iron and steel together with slag.

Iron-bearing materials include not only naturally occurring ferruginous and manganiferous minerals, but also certain industrial by-products, such as tap-cinder, rolling-mill scale, pyrites cinders, etc. The most important flux used is limestone. The value of fuels, apart from physical condition, caking power, and calorific effect, is determined chiefly by the amount and composition of the ash. Slags are always silicates, sometimes mixed with considerable amounts of ferroso-ferric oxide and phosphates.

The analytical investigation of ores, fluxes, fuel ashes, and slags is similar, so that they may be treated as a single group. All varieties of iron and steel, except those alloyed with rare metals, contain the same elements. Hence the subject matter of this section may be divided into two groups—the analysis of ores and the analysis of iron and steel.

I.—ANALYSIS OF ORES

The naturally occurring iron ores are mainly ferric oxide (red hæmatite), ferroso-ferric oxide (magnetic ore), hydrated oxide (brown hæmatite), or carbonates (spathic iron ore, clay-ironstone). The industrial residues worked up as ores are oxides (pyrites cinder), silicates mixed with much ferroso-ferric oxide (tap-cinder), or the latter alone (mill and forge scale).

The natural ores are never quite pure, but always contain foreign matter or are associated with other minerals, so that they usually contain silica, alumina, lime, baryta, magnesia, and alkalis. The usual tests are applicable for their detection, as also for the recognition of the presence of water and of organic matter.

Apart from the iron content, an ore is rendered more or less valuable by the presence or absence of certain other constituents. Manganese, on the one hand, often increases its value; such impurities as phosphates, sulphates, sulphur, copper, lead, zinc, antimony, arsenic, and titanium, on the other hand, may depreciate it considerably. Manganese, phosphorus, and sulphur are always determined during the analysis of iron ores, and the other impurities mentioned, together with cobalt, nickel, chromium, etc., may have to be looked for.

The presence of water, either as moisture or in chemical combination, of organic matter, and of carbonic acid, frequently affords information as to the variety of ore under examination.

Full and detailed analyses of ores, fluxes, and slags are not always required in iron-works. As a rule, such analyses are carried out only upon average samples of the various materials at fairly long intervals, in the investigation of new deposits, for calculating the blast furnace charges, for controlling the correctness of the calculations by analyses of the slag, or when ores are being purchased. As a rule, for instance, for controlling the quality of regular consignments of ore, it suffices to determine the chief valuable and injurious constituents—viz., iron, manganese, phosphorus, sulphur, and silica. Frequently it is not necessary to determine more than the iron, manganese, and insoluble residue. Volumetric methods are used whenever possible in works' laboratories. Gravimetric methods will, however, be considered first, because the separations, etc., involved in these have often to be carried out before the volumetric methods can be applied.

Sampling (*cf.* Vol. I., pp. 4-10).—Analyses cannot lead to results which are of practical value and do justice to both buyer and seller, unless the sample handed to the chemist really represents an average of the bulk from which it was drawn. It is often a matter of great difficulty, requiring considerable preliminary work, to secure this. The more finely divided and homogeneous the ore, the easier is the sampling. It then suffices to take 1 to 2 kg. of ore from each truck-load, collect the whole in a large box, and draw an average sample from the latter at intervals of, say, a week, or else after a certain agreed number of truck-loads has been delivered. Should the material, however, be irregular in size or in large lumps, it is much more difficult to draw a genuine average sample. In these circumstances the best course is to break pieces indiscriminately from lumps in every second, third, fourth, or fifth truck-load and to take a quantity of smaller material

in the same proportion to the lumps taken as is present in the bulk. The material thus obtained which may vary in weight from one hundredweight to over a ton, according to the weight of the material sampled, is then crushed to a uniform small size and sampled down.

This is effected as follows:—The material is placed on a suitable floor and spread out in a circle; starting from the circumference, it is then shovelled towards the centre until it is heaped in a cone. The cone is broken up, the material again spread out, and the operation repeated. After three such mixings, the evenly spread mass is divided into four quadrants, and two opposite quadrants, or one only, are taken aside, crushed finer, mixed, and again divided; and so on, until a quantity of only 1 to 2 kg. remains. This is then ground in an iron mortar in the laboratory, and further divided as above, so that a sample suitable for analysis is finally obtained. When the sample is hard, care must be taken to avoid its contamination with iron from the mortar.

The sample is prepared in quadruplicate: one portion is analysed, two portions delivered to the vendor, and the fourth kept in case of disputes.

Separate samples are usually taken for the determination of moisture, care being taken to avoid loss of moisture during crushing, etc.

The sample for analysis must be ground to pass a 60 or 80 mesh sieve before being weighed out, but ores which are difficult to dissolve should be ground finer in an agate mortar before weighing for analysis.

1. Gravimetric Analysis

Water or Loss on Ignition.—As a rule, it is merely necessary to determine the moisture which is expelled by drying a sample of the ore in the air-oven. For red hæmatites the best temperature is 110°, for brown hæmatites rich in manganese 100°, and for soft peaty ores 90°. If, in addition, it is required to determine the combined water, as in brown hæmatites, the sample is later on gradually brought to a red heat and ignited to constant weight; if carbonates or ferrous compounds are present, however, this method cannot be used, and the expelled water must be collected and weighed in a calcium chloride tube or other suitable absorbent. For this purpose, 1 g. of the finely powdered ore is placed in a boat and ignited in a combustion tube in a current of dried air; care must be taken to dry the air with the same substance (calcium chloride, sulphuric acid, phosphoric oxide) as is used in the absorption tube.

In the presence of organic matter it is customary to determine the loss on ignition which comprises the water, carbonic acid, and organic matter. In samples containing ferrous iron, a correction becomes necessary on account of its oxidation to ferric oxide.

The presence of organic matter also necessitates a preliminary ignition of the sample before solution, unless volatile constituents such as arsenic, sulphur, or carbonic acid are present; the weighed ore is ignited, at not too high a temperature, in an open porcelain crucible until the organic matter is destroyed.

Solution of the Ore.—The best solvent is fuming hydrochloric acid (sp. gr. 1·19), which is allowed to act on the finely powdered ore in an Erlenmeyer flask at 50°, the temperature being ultimately raised to the boiling point. The flask is most suitably warmed on a sand-bath or on a heated iron plate. In order to obtain all the iron in the ferric state, as is necessary for many determinations, a little nitric acid or potassium chlorate is added when the solution is nearing completion. If it is preferable to dissolve in sulphuric acid, dilute acid (1 to 1 by volume) is employed and the temperature kept at 100°.

If the undissolved residue is not white, but more or less coloured, it is probably silica contaminated by iron, and the iron is extracted from it by one of the following methods:—Either the residue is fused with sodium and potassium carbonates, or else it is dried, moistened in a platinum crucible with hydrofluoric and sulphuric acids, evaporated, and finally dissolved, the solution being added to the main bulk.

The solution of ores in sulphuric acid is greatly facilitated by previous reduction to the metallic state, which may be effected by hydrogen or coal gas, or by certain powdered metals. When a gaseous reducing agent is used, the weighed substance is placed in a boat in a combustion tube and the gas passed through at such a rate that a small flame continues to burn at the exit, while the tube is heated to redness by means of one or two burners; the reaction is completed after ten to fifteen minutes. The substance is then allowed to cool in a current of the gas and immediately dissolved in sulphuric acid (1 : 3).

In the second method, which is due to Donath and Jeller,[1] the finely powdered ore is mixed with an approximately equal volume of zinc dust in a porcelain crucible, covered with a layer of the same, and strongly ignited for from five to eight minutes with the lid on. The reaction is so vigorous that incandescence of the mixture, which may be observed through the walls of the crucible, sets in. In order that the reduction may be complete, ores containing ferrous iron must previously be moistened with ammonium nitrate and ignited, so as to oxidise all the iron to the ferric state. It is, of course, necessary to make a blank determination of iron in the zinc dust.

V. Jüptner[2] uses magnesium powder instead of zinc; for complete reduction four to six parts are mixed with one part of a comparatively refractory ore. Easily reducible ores, and slags poor in iron, need

[1] *Z. anal. Chem.*, 1886, **25**, 361; *Chem. News*, 1886, **54**, 73.
[2] *Chem. Zeit.*, 1894, **18**, 469; *J. Iron and Steel Inst.*, 1894, ii. 497.

only be mixed with an equal volume of magnesium, and a layer of as much magnesium again added in the crucible and the mixture ignited cautiously for five to ten minutes. A blank determination of the iron in the magnesium is also necessary.

Insoluble Residue and Silica.—When ores of known quality are being smelted, all that is usually required by way of control is the determination of the insoluble residue (silica, barytes, clay, and undecomposed mineral admixtures) and of the iron. For this purpose the solution, prepared as above, is diluted and filtered, and the residue ignited over the blowpipe in a platinum crucible and weighed. To determine the silica, the solution is twice evaporated to dryness, taken up with acid, diluted with water, heated, and the residue filtered and ignited. In evaporating, it is well to avoid excessive heating, since basic chlorides or ferric hydroxide, which redissolve with difficulty, tend to separate out. Moreover, ferric chloride is markedly volatile at comparatively low temperatures, and this may lead to low results in the subsequent determination of the iron. Since the silica thus obtained is never pure, the contents of the crucible, after weighing, should be evaporated with hydrofluoric and sulphuric acids, strongly ignited and reweighed. The loss in weight represents the pure silica.

Should the residue contain barytes, clay, or undecomposed ore, it must be fused with sodium and potassium carbonates, and the melt dissolved in warm water without the addition of acid.

The following is the procedure adopted by C. B. Murray,[1] of the American Steel Trust Laboratories, for the determination of silica in iron ores. One gram of the finely ground and dried ore is thoroughly fused with 12 to 15 g. of sodium carbonate. The melt is cooled and extracted in a beaker containing 200 c.c. of water, to which the same volume of strong hydrochloric acid is subsequently added. The solution of the melt is then evaporated to dryness, the residue taken up with 50 c.c. of hydrochloric acid, diluted with water, and the silica filtered off, ignited, and weighed.

The following modification is adopted for manganese ores. One gram of the ore is dissolved in 50 c.c. of hydrochloric acid, the solution boiled and filtered and the residue fused and added to the original solution; the whole is then treated as above.

Iron and Alumina.—Iron is seldom determined gravimetrically, but when alumina has to be determined, ferric and aluminium hydroxides are precipitated jointly from acid solution by a slight excess of ammonia and weighed together. The very general method of using a large excess of ammonia and then boiling it off is not to be recommended, because it is by no means easy to judge the point of neutrality; if boiling be continued beyond this point, some ammonium chloride is

[1] *Methods of Iron Analysis*, p. 50 (see Literature, p. 93).

apt to be dissociated and an equivalent amount of alumina brought into solution again, as has been shown both by Blum[1] and by Lunge.[2] It is preferable to precipitate with a small excess of ammonia, add ammonium chloride if necessary, allow to settle, and filter at once. In the presence of much lime, the precipitate should be dissolved and reprecipitated. The ignited and weighed precipitate, which contains all the phosphoric acid present as well as the oxides, is fused with acid potassium sulphate, the fused mass dissolved and the iron determined volumetrically. The alumina may then be found by difference, after the phosphoric acid has been separately determined. In order to determine alumina as such, the separation from iron may be carried out by pouring the hot solution of the joint precipitate, which should not be too dilute, into boiling sodium hydroxide solution, preferably contained in a platinum dish. The diluted liquid is then filtered, the filtrate acidified, and the alumina precipitated with a slight excess of ammonia. The precipitate must be redissolved and reprecipitated, in order to free it from fixed alkali; it will contain all the phosphoric acid, which must also be determined and deducted if present. The alumina precipitate should also be tested for titanic acid and a correction applied if this is present. Iron together with any titanium present may also be separated from the weighed precipitate by treating the cold acid solution with excess of a 6 per cent. aqueous solution of "cupferron." The precipitate, after washing well with 10 per cent. hydrochloric acid, is ignited cautiously at first, then strongly. The residue consists of oxides of iron and titanium. From weakly acid solutions "cupferron" precipitates iron and copper if present, but nickel, cobalt, aluminium, chromium, zinc, manganese and cadmium remain in solution (*cf.* p. 82).

The separation of iron and alumina is greatly facilitated by the ether extraction method proposed by Rothe,[3] which is specially adapted to the separation of large quantities of iron from small quantities of manganese, chromium, nickel, aluminium, copper, vanadium, uranium and titanium. It is based on the fact that ferric chloride in presence of hydrochloric acid and ether gives a compound which is easily soluble in the latter, whereas the chlorides of the other metals enumerated do not possess this property. Hence it is possible to extract ferric chloride quantitatively by means of ether and so to remove large quantities of iron. The essential conditions for carrying out this method are—(1) that the iron be present as ferric chloride; (2) that an excess of acid of definite strength be present; and (3) that there be no superfluous water.

[1] *Z. anal. Chem.*, 1888, **27**, 19.
[2] *Z. angew. Chem.*, 1889, **2**, 634; *J. Soc. Chem. Ind.*, 1890, **9**, 111.
[3] Cf. *Chem. News*, 1896, **74**, 296.

Five grams of the ore is dissolved in hydrochloric acid, evaporated to dryness, taken up with hydrochloric acid and the solution filtered; the washed residue is then fused, the silica removed, and the alumina precipitated in the filtrate by ammonia. If this precipitate contains iron, it is dissolved in hydrochloric acid and added to the bulk. The solution is then oxidised, if necessary, by adding a few drops of strong nitric acid, concentrated to about 10 c.c., poured into a separating funnel and rinsed with cold hydrochloric acid of sp. gr. 1·124 (at 19°), until the total volume reaches 55 to 60 c.c. It is important that the solution should be quite clear and free from basic precipitates.

An equal volume of ether is now added, the liquids are brought into contact by thorough shaking, the whole being kept cold, preferably under a water tap; the funnel is allowed to stand until the layers have completely separated and the lower layer is run out into a second funnel for treatment with a fresh quantity of ether.

The solution, which is now practically free from iron, is evaporated to dryness, taken up with hot water and a few drops of hydrochloric acid and heated to boiling, after the addition of 1 c.c. of concentrated acetic acid and 1 g. of sodium acetate; 2 c.c. of a saturated solution of sodium phosphate is then added to precipitate the aluminium. The precipitate, which, even after washing with hot water, is apt to retain manganese and copper, is redissolved in a little hydrochloric acid, evaporated to dryness, taken up with a few cubic centimetres of water, boiled for some time with 2 or 3 g. of aluminium-free sodium hydroxide, made up to 250 c.c., and filtered through a dry filter paper. Two hundred c.c. of the filtrate, corresponding to 4 g. of ore, is acidified with acetic acid and the aluminium precipitated as phosphate. The well-washed precipitate is ignited, and then contains 41·85 per cent. of Al_2O_3.

Manganese.—In works' laboratories manganese is generally determined volumetrically, especially when manganese or manganese and iron only have to be determined. In conducting a complete analysis, however, a gravimetric determination will be found more suitable; this necessitates the previous removal of the iron and alumina. The following five methods are available for this separation:—

Separation of Manganese from Iron and Alumina.—1. *Acetate Method.*[1] The oxidised hydrochloric acid solution of 1 to 2 g. of the ore (or more if the content of manganese be very low) is evaporated to dryness, redissolved in the least possible quantity of hot hydrochloric acid, allowed to cool, diluted, heated nearly to boiling, and filtered. The completely cooled filtrate, the bulk of which should not exceed 250 c.c., is partially neutralised to a deep red colour with ammonia and neutralisation completed with ammonium carbonate; if a permanent precipitate is formed, owing to the addition of an excess of this

[1] *Cf.* Brearley, *Chem. News*, 1897, **75**, 253; 1897, **76**, 49, 165, 175, 210, 222.

reagent, it is redissolved in hydrochloric acid and the neutralisation recommenced. It is convenient to have a strong and a dilute solution of ammonium carbonate and to use the latter towards the end of the process; in the earlier stages, solid powdered ammonium carbonate may be used with advantage. About 0·75 g. of ammonium acetate for each gram of iron is then added to the deep red solution, the volume of which is made up to about 1000 c.c. by the addition of boiling water, and the whole placed on a hot plate and boiled for one or two minutes. Prolonged boiling renders the precipitate slimy and difficult to filter. In many works' laboratories the sodium salts are preferred for neutralisation and precipitation.

The precipitated basic ferric acetate is allowed to settle, the colourless solution decanted off through a large filter, and the precipitate washed by decantation with hot water in which a little ammonium acetate is dissolved. The precipitate contains all the aluminium and phosphoric acid present, in addition to the iron; it may be used for the volumetric determination of the iron.

If the neutralisation, which requires some little practice and patience, has been properly carried out, a single separation may suffice. If special accuracy is required, or when the operator lacks experience with the method, it is desirable to redissolve the iron precipitate, repeat the separation, and unite the filtrates.

The voluminous basic acetates of iron and aluminium are difficult to wash, and are apt to pass through the filter towards the end of the filtration. Washing may be entirely circumvented by resorting to the method of partial filtration, which is carried out as follows:—The precipitation is effected in a large pear-shaped flask, in which the solution, diluted to not quite 1000 c.c., is heated directly by a large burner, without any interposed wire gauze. After adding the precipitant and boiling briskly for half a minute, the contents are poured into a graduated litre flask and made up with boiling water and the temperature recorded. The solution is then filtered through a large pleated filter paper until 750 c.c. has been collected, the operation being so rapidly performed that the liquid is not cooled down by more than a few degrees during filtration. The solution should be reheated to the original temperature in order to obtain the correct volume. The filtrate is used for the determination of the manganese, the residual liquid and precipitate being discarded.

For specially accurate work, it is desirable to take into account the volume of the precipitate which may be assumed to displace 0·7 c.c. for every 1 g. of iron.

2. *Ammonium Carbonate Method.* The oxidised solution of the ore in hydrochloric acid is evaporated to dryness, and the residue is taken up with acid and hot water. About 5 g. of ammonium

chloride for every 1 g. of ore is then added, together with at least 250 c.c. of water per gram of ore. The solution is neutralised with dilute ammonium carbonate solution, which is added until the liquid just begins to become turbid; should a permanent precipitate be formed, a few drops of acetic acid are added and the solution allowed to stand until it becomes clear. On heating to boiling, and continuing to boil until all the carbon dioxide has been driven off, a precipitate of basic iron and aluminium salts, which settles readily, is formed. This is somewhat difficult to wash, and may therefore be separated by partial filtration, as described above. If the supernatant liquid is not colourless, but slightly yellow, the iron has not been completely precipitated, and a few drops of ammonia must be added before filtering, but not enough to be noticeable by the smell.

The filtrate should be faintly acid and colourless; it is acidified slightly to keep the manganese in solution, boiled down to a small bulk, and a few drops of ammonia added, any ferric or aluminium hydroxide which is precipitated being filtered off and tested for traces of manganese. The determination of the manganese in the bulk is then carried out by the usual methods.

3. *Sulphate Method.* The chief advantage of this method, which is due to Kessler,[1] is that the precipitate is easily washed. The oxidised hydrochloric acid solution after the separation of silica if a gravimetric method is to be used, is approximately neutralised with ammonia, and ammonium carbonate added to incipient turbidity. So long as the liquid is dark brown and of acid reaction, no precipitation of manganese need be feared. One gram of ammonium sulphate for every gram of iron is then added to the cold solution, when a brown precipitate of basic ferric sulphate is formed. Should the precipitate be of comparatively light colour, it indicates that the neutralisation is incomplete and that iron remains in solution. The precipitate is very bulky, and filters with difficulty at first, but gives no trouble in washing. The aluminium remains partially in the filtrate, but can be removed by adding a few drops of ammonium acetate and boiling.

4. *Zinc Oxide Method.*[2] One to two grams of iron ore, or 0·5 g. of manganese ore, is dissolved in hydrochloric acid, filtered, oxidised with potassium chlorate or hydrogen peroxide, boiled till free from chlorine, and diluted to 400 or 800 c.c. in a measuring cylinder, according to the amount of iron present. Zinc oxide, finely powdered and suspended in water, is then added in small quantities at a time with thorough agitation, until the precipitated ferric hydroxide suddenly coagulates. On settling, the liquid will be found to be colourless. It is

[1] *Z. anal. Chem.*, 1872, **11**, 258; *J. Iron and Steel Inst.*, 1880, i. 353.

[2] *Cf.* Volhard, *Annalen*, 1879, **198**, 318; *Chem. News*, 1879, **40**, 207; *J. Iron and Steel Inst.*, 1880, i. 355.

made up to a known volume, shaken, and subjected to partial filtration. Barium carbonate is frequently used instead of zinc oxide.

5. *Ether Method.* Rothe's method for separating iron from aluminium, described on p. 6, is sometimes employed with advantage for separating iron from manganese.

Determination of Manganese.—1. *Manganese Peroxide Method.* To precipitate manganese as hydrated peroxide, bromine, bromine water, brominated air, or hydrogen peroxide may be used. The iron-free filtrate is nearly neutralised with ammonia or sodium carbonate, evaporated down to about 250 c.c., cooled to 50°, treated with 2 to 3 c.c. of bromine or 50 c.c. of bromine water and well stirred. After allowing to stand for a few minutes, 20 to 25 c.c. of ammonia (1 : 1) is added, the solution again stirred vigorously and then boiled for some minutes. The precipitate is allowed to settle, the supernatant liquid decanted through a filter paper, on which the precipitate is afterwards collected and washed. The filter is then burnt and the precipitate ignited to Mn_3O_4 and weighed. The precipitate may be contaminated with iron, nickel, cobalt, zinc, etc., and should be dissolved in a few c.c. of hydrochloric acid, a slight excess of ammonium acetate added, sulphuretted hydrogen passed to saturation, and the liquid boiled and filtered. The filtrate is boiled until free from sulphuretted hydrogen, oxidised with bromine water, the manganese precipitated with ammonia as above, ignited to Mn_3O_4 and weighed. If the sulphide precipitate is small it may be ignited and weighed, the weight being deducted from the weight of the impure Mn_3O_4 first obtained, thus obviating the necessity of a second precipitation of the manganese.

The precipitation of manganese peroxide may be carried out by Wolff's method,[1] for which the apparatus shown in Fig. 1 may be used. A current of air is drawn by a filter-pump, through the bottle *a*, which contains bromine water with some pure bromine at the bottom, and thence into a large conical flask, *d*, in which the filtrate containing the manganese is placed; this filtrate is not previously concentrated, but is made strongly ammoniacal. The rubber surfaces exposed to bromine should be as small as possible. When the precipitated peroxide is seen to have separated out, the current of air is stopped; fifteen to twenty minutes' treatment suffices even for the considerable amounts of manganese which occur in pyrolusite or ferromanganese. The liquid must remain distinctly ammoniacal from start to finish for the precipitation to be complete and to avoid the formation of nitrogen bromide. After the precipitation, the bottle *a* is replaced by one containing ammoniacal water, and air is passed through the liquid for fifteen minutes more, when the precipitate settles readily; it is then filtered off, washed with cold water, ignited to Mn_3O_4 and treated as above for impurities.

[1] *Z. anal. Chem.*, 1883, **22**, 520.

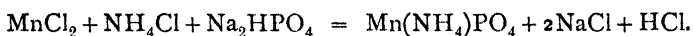
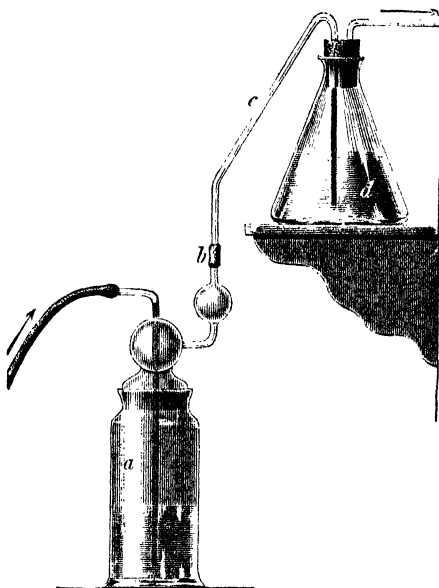
Instead of the method described above, brominated hydrochloric acid may be added direct to the manganese solution, followed by treatment with ammonia.

2. *Manganese Sulphide Method.* This method is seldom adopted. The manganese acetate solution is first treated with sulphuretted hydrogen to precipitate cobalt, nickel, and zinc, and the filtrate is made strongly ammoniacal. Yellow ammonium sulphide is added to the boiling solution, the boiling continued for a few minutes, and the precipitate allowed to settle; it should consist of green anhydrous manganese sulphide, and is at once filtered off and washed with water containing ammonium sulphide. The filtrate is apt to retain inconsiderable amounts of manganese. The filter paper and precipitate are burnt wet, roasted to Mn_3O_4, and finally ignited strongly for half an hour.

In a complete analysis of an iron or manganese ore, the filtrate from the manganese sulphide can be used for the determination of the alkaline earths.

FIG. 1.

3. *Manganese Ammonium Phosphate Method.* This method, devised by Gibbs,[1] has been improved by Böttger.[2] A quantity of ammonium chloride, corresponding to five to ten times the quantity, in molecular proportion, of the manganese present, is added to the neutralised solution of the manganese. The liquid is heated to boiling in a porcelain or platinum dish, and a considerable excess of 12 per cent. solution of di-sodium phosphate is added. The precipitation takes place in accordance with the equation:—

$$MnCl_2 + NH_4Cl + Na_2HPO_4 = Mn(NH_4)PO_4 + 2NaCl + HCl.$$

To ensure complete precipitation, the liberated acid is neutralised with ammonia and the liquid heated until the precipitate changes from the amorphous form to glittering pink crystals. These are filtered off, thoroughly washed with hot water, and ignited over the blowpipe to manganese pyrophosphate.

[1] *Z. anal. Chem.*, 1868, **7**, 101; *Chem. News*, 1868, **17**, 195.
[2] *Ber.*, 1900, **33**, 1019; *Chem. News*, 1900, **82**, 247.

Chromium.—Whereas ordinary chromiferous iron ores dissolve without difficulty in hydrochloric acid, chromite (chrome iron ore) has to be rendered soluble by fusion. Half a gram of the latter, previously ground fine and sieved through linen, is mixed in a silver dish with 5 to 6 g. of sodium hydroxide, with a superimposed layer of 3 to 4 g. of sodium peroxide and heated very gradually with a luminous flame.[1] After five minutes, the edges of the sodium hydroxide should begin to melt, and after ten minutes the whole mass; the fusion is then continued for an hour, the melt allowed to cool and extracted with water. Silver is not proof against the action of sodium peroxide, and therefore nickel crucibles are frequently used, or, when contamination with nickel is to be avoided, copper crucibles.[2] The solution of the melt is yellow or green, according to the amount of manganese present; if it is green, small quantities of sodium peroxide (0·3 to 0·6 g.) are added very gradually until the sodium manganate colour disappears and the solution has the clear yellow colour of sodium chromate. To remove the excess of peroxide, carbon dioxide is passed into the solution for an hour and the liquid allowed to stand in a warm place for fifteen minutes. The entire residue should be flocculent, if the fusion is complete.

An alternative method, and one particularly adapted to the determination of chromic oxide in chromite, consists in heating for one hour an intimate admixture of the finely ground mineral (0·2 g.) with 4 g. of anhydrous sodium hydroxide and 1·7 g. of magnesia. The mixture is preferably made in a warm dry mortar and subsequently transferred to the crucible. The fused mass is cooled and extracted with a small quantity of boiling water, and the solution boiled to decompose the sodium manganate and ferrate which may be present. The liquid is then filtered and the residue washed; the filtrate should be yellow and quite clear.

The chromium is determined gravimetrically in the solution obtained by either of the above methods, after acidifying the solution and reducing with sulphurous acid. The excess of the latter is removed by boiling and the chromium precipitated by the addition of a slight excess of ammonia to the boiling solution. The precipitate, after being thoroughly washed, is ignited and weighed as Cr_2O_3. It may be examined for impurities by fusion with a small quantity of sodium carbonate and a trace of sodium nitrate and extracting with water (Lambert).

McIvor and Dittmar[3] melt equal parts of borax and fusion mixture

[1] Spüller and Kalman, *Chem. Zeit.*, 1893, **17**, 880, 1207, 1360; 1897, **21**, 3; *J. Iron and Steel Inst.*, 1893, ii. 537; 1894, i. 614. *Cf.* Spüller and Brenner, *Stahl u. Eisen*, 1897, **17**, 101; *J. Iron and Steel Inst.*, 1897, i. 570.

[2] *Cf.* McKenna, *Eng. and Min. J.*, 1898, p. 607.

[3] *Chem. News*, 1900, **82**, 97.

together, add 4 g. of this product to 0·5 g. of the finely powdered ore, and fuse; after cooling, 2 to 5 g. of fusion mixture is added and the mass fused again. The melt is transferred to a platinum dish, extracted with hot water, filtered, and the residue washed with hot water; the filtrate is acidified with acetic acid, precipitated with lead acetate, and the chromium weighed as $PbCrO_4$.

When the ore is soluble in hydrochloric acid, 2·0 g. is taken for analysis. The solution is deprived of the bulk of its ferric chloride by the ether method (p. 6) (according to Carnot,[1] this may be omitted), diluted, heated to 100°, treated with a few cubic centimetres of hydrogen peroxide and an excess of ammonia, and boiled; chromium thus remains in solution as ammonium chromate, whilst other heavy metals are precipitated. The precipitate is redissolved and the operation repeated. The combined filtrates are slightly acidified with hydrochloric acid and reduced with hydrogen peroxide, sulphuretted hydrogen being passed in to destroy excess of the latter. Chromium hydroxide is then precipitated by boiling with ammonia, filtered off, washed, ignited, and weighed as Cr_2O_3.

Zinc.—According to the commonly adopted method, iron is removed as hydroxide or basic acetate and the zinc precipitated from the hot filtrate by passing in sulphuretted hydrogen in presence of acetic acid. Cobalt and nickel are not completely kept in solution under these conditions, and in order to obtain pure zinc sulphide it is necessary to resort to repeated reprecipitations.

The method is greatly improved when, as suggested by Hampe, formic acid is substituted for acetic acid. The following method for zinciferous iron ores, which often contain lead as well, has been worked out by Kinder.[2] Five grams of the ore is digested with water and dissolved in hydrochloric acid in a capacious, covered porcelain dish, 20 to 25 c.c. of sulphuric acid (1 : 2 by volume) added, and the whole evaporated until fumes of sulphuric anhydride are evolved. The residue, after cooling, is taken up with water, filtered, the filtrate diluted to 300 to 400 c.c., and saturated with sulphuretted hydrogen. Copper sulphide, if formed, is filtered off, and 25 c.c. of ammonium formate solution and 15 c.c. of formic acid added; if the correct proportion of sulphuric acid has been used, the zinc sulphide should then separate as a flocculent, almost white, precipitate; but in case an excess has been employed, it is safer to neutralise the greater part of the free sulphuric acid with ammonia before adding the ammonium formate. If much zinc is present, more sulphuretted hydrogen is passed into the warmed liquid. If the zinc sulphide comes down discoloured, it is dissolved in hydrochloric acid, the solution made alkaline with ammonia, then

[1] *Z. anal. Chem.*, 1890, **29**, 336.
[2] *Stahl u. Eisen*, 1896, **16**, 675; *J. Iron and Steel Inst.*, 1896, ii. 452.

acidified with formic acid, an excess of 15 c.c. being added, and the zinc reprecipitated by sulphuretted hydrogen as above.

Zinc sulphide may be weighed as such, after having been ignited in a boat or in a Rose's crucible in a current of sulphuretted hydrogen. Alternatively the sulphide may be dissolved in hydrochloric acid and precipitated in the cold with sodium carbonate. The precipitate thus formed is gelatinous, but filters well; after washing four times by decantation and fifteen times on the filter it is free from salts, and may then be ignited and weighed as ZnO.

Nickel and Cobalt.—These metals are precipitated together by ammonium sulphide in the filtrates from the iron, aluminium, and zinc; manganese, if present, will be precipitated with them. On treating the precipitate with dilute hydrochloric acid (1 : 6), the manganese sulphide is dissolved. The residual sulphides of cobalt and nickel are filtered off, washed, and ignited to oxides, or else dissolved, and the contained metals determined electrolytically. The oxides must always be tested for iron and manganese. Cobalt and nickel need not usually be separated, since cobalt rarely occurs in iron ores to any appreciable extent. Should a separation be required, it is best carried out either by the dimethylglyoxime method (p. 66) or by the nitroso-β-naphthol method (p. 70). The determination of nickel is more fully dealt with in the analysis of iron and steel (*cf.* pp. 65-69).

Lime and Magnesia.—These remain in the filtrates from the treatment with ammonium sulphide, and are precipitated as calcium oxalate and magnesium ammonium phosphate respectively, in the usual way (*cf.* Vol. I., pp. 510-513).

Barium.—Barium may be present in iron ores as heavy spar, and in blast furnace slags as barium sulphide. If present as heavy spar it remains with the undissolved siliceous residue, and is extracted by fusion with alkali carbonate (see Sulphur, p. 20). When present as sulphide it may partly remain with the insoluble residue and partly pass into solution, and may be precipitated completely from solution by the addition of sulphuric acid.

Alkalis.—Under circumstances which permit of the practice of recovering potash from blast furnace waste gases, the alkalis may have to be determined in ores, fuel ashes, fluxes, slags, flue dust, etc. The usual methods of obtaining a solution, separating all other metals by means of ammonium salts, weighing as mixed sulphates, and separating the potassium as platinichloride or perchlorate, may be adopted (*cf.* pp. 399 and 404).

For substances not completely decomposed by acids, Laurence Smith's method[1] of heating with ammonium chloride and calcium carbonate may be used as a preliminary operation to solution.

[1] *A Text-book of Assaying*, C. and J. J. Beringer, 1921, p. 333.

Copper, Lead, Arsenic, Antimony.—These impurities may be determined in the same portion. Ten grams of the ore is dissolved in hydrochloric acid, with repeated addition of a little nitric acid, the solution filtered and either evaporated or the bulk of the iron removed by the ether extraction method. The residue is fused with sodium carbonate and the extract added to the main solution. The iron is then reduced to the ferrous state, and sulphuretted hydrogen passed in. If sulphur dioxide acid is employed to reduce the iron, the boiling requisite to remove excess of the gas from the solution should not be prolonged, otherwise loss of arsenic may result. The precipitate is washed with dilute sulphuretted hydrogen solution and digested with sodium sulphide. Antimony and arsenic sulphides are precipitated from the filtrate by hydrochloric acid, filtered off, and warmed with hydrochloric acid and potassium chlorate; tartaric acid, magnesia mixture, and ammonia are then added to the filtered solution. On standing for twenty-four hours, the arsenic is precipitated as magnesium ammonium arsenate, which is ignited and weighed as $Mg_2As_2O_7$. The filtrate is acidified and treated with sulphuretted hydrogen, the precipitated antimony sulphide filtered, washed, dissolved in the least possible volume of yellow ammonium sulphide, the solution evaporated to dryness in a porcelain crucible, and the residue repeatedly evaporated with fuming nitric acid until sulphur is completely oxidised, ignited and weighed as Sb_2O_4; this contains 78·97 per cent. Sb. The black sulphides insoluble in sodium sulphide are dissolved in nitric acid, evaporated down with a little sulphuric acid, and treated with alcohol. Lead sulphate is thus precipitated and weighed as such. From the filtrate, copper sulphide may be precipitated and ignited to the oxide, or the copper may be separated electrolytically.

When arsenic is determined separately, copper, lead, and antimony may be determined as follows:—The bulk of the iron is removed from the original solution of ore after concentrating by means of ether (*cf.* p. 6). The insoluble residue is decomposed by fusion, as above, the filtered extract added to the acid solution, and the whole evaporated to dryness, when the arsenic is expelled as the trichloride. If nitric acid or potassium chlorate has been used in preparing the solution the arsenic will be in the pentavalent condition, and must be reduced with sulphur dioxide before evaporating to dryness. On taking up with dilute hydrochloric acid and passing in sulphuretted hydrogen, the sulphides of copper, lead, and antimony are precipitated; the subsequent operations are carried out as described above.

The determination of arsenic alone is conveniently carried out by Ledebur's method. Ten grams of the ore is treated, with frequent agitation, with 120 c.c. of hydrochloric acid of sp. gr. 1·19; when dissolved as far as possible, 2 to 4 c.c. of bromine is added, and the

liquid warmed up gradually until nearly all the bromine has volatilised. The clear liquid is then poured off, the residue filtered off and washed, and the whole of the solution thus obtained placed in the flask *a* (Fig. 2), together with a solution of 15 g. of arsenic-free ferrous chloride in 60 c.c. of hydrochloric acid of sp. gr. 1·124; the solution is then cautiously distilled over a rose burner. When about 40 c.c. remain, 50 c.c. of hydrochloric acid is added and the distillation continued down to a residual volume of 40 c.c. The distillate, which contains all the arsenic, is treated with sulphuretted hydrogen at about 70°. After standing for several hours, the arsenic sulphide is filtered off, washed till the filtrate is neutral, dissolved in ammonium carbonate, reprecipitated by hydrochloric acid and sulphuretted hydrogen water, the precipitate collected on a tared filter paper, and washed till free from chlorides. The filter is then dried, allowed to cool in a desiccator, and the arsenic weighed as trisulphide; this contains 60·93 per cent. of arsenic.

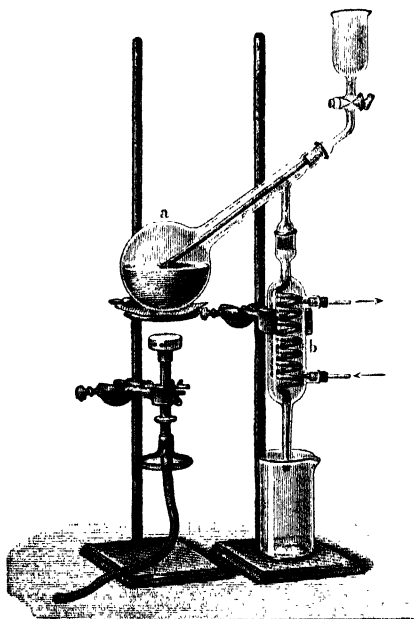
Fig. 2.

Phosphorus.—The method now in general use for determining phosphoric acid is by precipitation as ammonium phospho-molybdate, $(NH_4)_3PO_4 . 12MoO_3$. In order to secure correct results, it is necessary to take into account the conditions under which quantitative precipitation takes place. The various points to be considered have been summarised and the results of Fresenius and others confirmed by Hundeshagen;[1] his main conclusions are as follows:—

(1) Free hydrochloric or sulphuric acids, free nitric acid (over 80 molecules to 1 molecule of phosphoric acid), and salts of polybasic acids (especially sulphuric and boric acids) prevent complete precipitation.

(2) Free nitric acid (26 to 80 molecules per molecule of phosphoric acid) retards precipitation.

(3) Free nitric acid (less than 26 molecules) and salts of monobasic acids (chlorides, bromides, etc.) have no harmful action.

[1] *Z. anal. Chem.*, 1889, **28**, 141; *Chem. News*, 1889, **60**, 169, 177.

(4) Ammonium nitrate greatly accelerates precipitation, so much so that 0·5 g. brings down all the phosphorus, unless present in mere traces, in a few minutes.

(5) High temperatures favour precipitation. With only 0·05 g. of phosphoric acid in 100 c.c., the precipitate is instantly formed at boiling temperature, especially on rubbing with a glass rod. Precipitates from hot solutions are crystalline and filter better than those from cold solutions.

(6) There must be at least twice as much molybdic acid as is theoretically required—that is, at least 24 molecules to 1 of phosphoric acid.

(7) Cold water, very dilute acids, and solutions of ammonium salts have a slight solvent action on the precipitate.

It is important that the liquid to be precipitated should be free from silicic acid, since this yields a compound with molybdic acid closely resembling the phospho-molybdate. Also, all the phosphorus must be present as phosphoric acid, since the lower oxides of phosphorus are not completely precipitated. After drying at 130° to 150°, the precipitate consists of $(NH_4)_3PO_4 . 12MoO_3$, and contains 3·782 per cent. P_2O_5, or 1·651 per cent. of phosphorus; owing to slight decomposition it is usual in practice to take 1·63 as the percentage of phosphorus.

Limonite must be ignited before solution to remove the organic matter which is always present, as this interferes with the complete precipitation of the phosphoric acid.

The determination of phosphorus is carried out as follows:—From 0·5 to 10 g. of the sample is weighed out according to the approximate proportion of phosphorus present; for basic slag 0·5 g.; for calcareous ironstone, limonite, and puddle slag 1 g.; for red and brown hæmatites and magnetic ores 5 g.; and for ores for acid pig irons 10 g. The weighed portion is dissolved in concentrated hydrochloric acid, the solution evaporated to dryness, taken up with hydrochloric acid and evaporated down again, baked, and the residue digested with 10 to 20 c.c. of nitric acid of sp. gr. 1·2. After diluting, warming, and filtering, and washing the residue with water containing nitric acid, the volume of the liquid should not exceed 20 c.c. if 1 g. of the sample was taken, or 50 c.c. for larger quantities. The solution is then neutralised with ammonia, 1 g. of ammonium nitrate added, the liquid heated to about 80°, and precipitated with 25 to 50 c.c. of ammonium molybdate solution prepared as follows: 150 g. of pure ammonium molybdate is dissolved in water, 450 g. of ammonium nitrate is then added to the solution, the whole diluted to 1000 c.c., poured into 1000 c.c. of nitric acid of sp. gr. 1·19, allowed to stand for twenty-four hours at 35°, and then filtered. The precipitation of the phosphorus may be regarded as complete after

standing for half an hour at 70° to 80°. The phospho-molybdate is then filtered off and washed till free from iron with water containing 5 per cent. by volume of concentrated nitric acid. The precipitate is then dissolved in warm dilute ammonia; the solution is collected in the vessel in which the original precipitation was effected, and the filter paper washed with a 2·5 per cent. solution of ammonia. Hydrochloric acid is added to the solution thus obtained to just short of reprecipitation, then 2 c.c. of magnesia mixture and one-third of the whole volume of ammonia; the liquid is well stirred and allowed to stand for fifteen minutes. In order to obtain the characteristic crystalline precipitate of the composition $MgNH_4PO_4 . 6H_2O$ the precipitation should be made from a hot solution.[1] Very small amounts of phosphate may need longer standing; in any case, the precipitate should settle clear out of the liquid. The magnesium precipitate is filtered off, washed with dilute ammonia, burnt wet in a platinum crucible, ignited till perfectly white, and weighed as $Mg_2P_2O_7$. If it is not quite white, a few drops of nitric acid may be added, evaporated off, and the ignition repeated.

With arsenical ores certain precautions are necessary, since both the molybdate and the magnesium precipitates will contain arsenic. If there is but little arsenic, advantage may be taken of the fact that magnesium ammonium arsenate requires much more time to separate out—at least twelve hours—than the phosphate. When an appreciable proportion of arsenic is present, the magnesium precipitate is dissolved in hydrochloric acid, the solution treated with sulphuretted hydrogen at 70°, the arsenic sulphide filtered off, the filtrate boiled down with a little potassium chlorate and reprecipitated with magnesia mixture.

Titanium, if present, also gives a precipitate with molybdic acid. The ore must then be fused with four times its weight of fusion mixture and the melt extracted with water, when titanium dioxide remains undissolved. The filtrate is freed from silica by evaporation with hydrochloric acid, and baking, and is then treated as above.

Instead of converting it into magnesium ammonium phosphate, the molybdate precipitate may be weighed direct. This may be carried out by filtering on to a carefully tared filter paper, drying and weighing the whole or, if a hard surfaced filter paper is used the precipitate may be brushed off with a suitable camel hair brush. In some laboratories an ammoniacal solution of the molybdate precipitate is evaporated till nearly free from ammonia, an adequate quantity of dilute nitric acid added, and the evaporation continued. When the mass becomes pasty, it is cautiously taken to dryness over an asbestos sheet or wire

[1] Gooch, *Z. anorg. Chem.*, 1899, **20**, 135.

gauze, and heated to 130° to 150° until a watch-glass laid on the dish shows no sublimate after half a minute. The residue is then allowed to cool in a desiccator and weighed.

Ores containing heavy spar must invariably be treated by fusion or by solution in acid and subsequent fusion of the residue, since the latter sometimes retains more than half of the total phosphorus. It is generally advisable to examine insoluble residues for phosphorus.

The following is a brief description of the method of determining the phosphorus in iron ores in use at the laboratory of the Monongahela Furnace, McKeesport, Pa.[1]

From 2 to 5 g. of the ore is digested with 75 to 150 c.c. of concentrated hydrochloric acid and the solution evaporated to hard dryness. About 100 c.c. of strong hydrochloric acid is poured on the residue and the mixture boiled until the solution is concentrated to about half this volume; water is then added and the diluted solution filtered, keeping the volume of the filtrate as small as is convenient. The solution is then twice evaporated with nitric acid to get rid of the hydrochloric acid. The insoluble residue is ignited and the silica driven off with hydrofluoric acid. The residue is fused with sodium carbonate, dissolved in nitric acid, and the solution filtered into the main solution. The whole is then placed in a 500 c.c. Erlenmeyer flask and dilute ammonia added until the solution becomes pasty and smells ammoniacal; the precipitate is then dissolved in a slight excess of nitric acid, and the solution heated up to 80°, when 40 c.c. of the molybdate solution is added. The solution is agitated by a current of air for about five minutes, filtered, while still warm, on a tared filter paper, and after washing thoroughly with five per cent. nitric acid, the yellow precipitate of ammonium phospho-molybdate is dried and weighed.

Sulphur and Sulphates.—In many ores only the total sulphur present is required, but in some it is necessary to determine the soluble sulphate sulphur, representing mainly calcium sulphate, but sometimes also partially oxidised pyrites in the form of sulphates of iron, zinc, etc.; the pyritic or sulphide sulphur; and the insoluble sulphate sulphur in the form of barytes.

Total Sulphur.—In this determination it is preferable to decompose the ore by fusion rather than to dissolve it in acid. Three grams of ore is mixed with an equal quantity of sodium carbonate containing 10 per cent. of potassium nitrate, gradually heated to a red heat in a platinum crucible, and fused for some time. The melt is extracted with hot water, the filtrate evaporated to dryness with hydrochloric acid, and baked, the residue taken up with hydrochloric acid and hot water, the silica filtered off, the clear acidified solution precipitated with

[1] *Methods of Iron Analysis*, p. 12 (see Literature, p. 93).

barium chloride, and the total sulphur weighed as barium sulphate in the usual way (*cf.* Vol. I., pp. 367-9). A blank determination using the same reagents is necessary.

Soluble Sulphur.—From 3 to 10 g. of the finely divided sample is extracted several times with cold water until the extract contains no sulphates. The extract is then acidified with hydrochloric acid and the sulphur precipitated with barium chloride in the usual way.

Sulphide Sulphur.—The residue from above is treated with nitric acid, followed by hydrochloric acid and heated until decomposition is complete. It is evaporated to dryness, taken up with hydrochloric acid diluted, filtered, and barium chloride added to the filtrate.

Insoluble Sulphur.—The residue from above will contain any barytes present. If not much silica is present, it should be treated with hydrofluoric acid, evaporated to dryness and fused with pure sodium carbonate. The fused mass is extracted with hot water and filtered. The filtrate is just acidified with hydrochloric acid and barium chloride added. The residue will consist of barium carbonate, and may be dissolved in a little hydrochloric acid and sulphuric acid added to precipitate the barium. The weights of the two barium sulphate precipitates should be the same, and represent the barytes present in the ore.

Titanium.—The determination of titanium,[1] which frequently occurs in iron ores, is somewhat complicated, but has been facilitated by the introduction of the ether separation process. The following method, described by Ledebur, is employed to a considerable extent:—

Five grams of the ore is dissolved in hydrochloric acid, when part of the titanium is left behind in the residue. The solution is extracted with ether to remove the iron, as described on p. 6. Phosphoric and titanic acids remain in the aqueous solution, though the latter may separate out in flocculent particles. Meanwhile the residue is melted with fusion mixture, the silica separated in the usual way, ignited, and evaporated with hydrofluoric and sulphuric acids, any residue of titanium dioxide being fused with acid potassium sulphate. The separated solution and the extracts of the two melts are then united, neutralised, and boiled with sodium acetate, whereby any residual iron, together with alumina, phosphoric acid, and titanic acid, are separated from the chlorides of the other metals present. The basic acetate precipitate, after washing with hot water, is again fused with fusion mixture and lixiviated; the residue then contains ferric oxide, alumina, and all the titanic acid. It is washed, dried, and again fused with not less than twelve times its weight of acid potassium sulphate, until every particle is dissolved. The melt is dissolved in cold water, treated with

[1] See *Titanium, with special reference to the Analysis of Titaniferous Substances*, by W. H. Thornton. Chemical Catalog Co.

sulphuretted hydrogen, filtered from any precipitate of copper or platinum sulphide, and boiled in a conical flask for an hour. The titanium dioxide is thus precipitated and is filtered off, washed, dried, ignited, and weighed.

In another method of dealing with the solution from the sulphate fusion, after precipitation of copper as sulphide and filtering, a little tartaric acid is added, the solution made ammoniacal and treated with more sulphuretted hydrogen. The ferrous sulphide is filtered off, the filtrate acidified with dilute sulphuric acid and the titanium precipitated with cupferron in the cold (see p. 82).

Ledebur has proposed to separate the bulk of the iron from titanium by reducing the ore in a current of hydrogen and dissolving the metallic iron formed in sulphuric acid (1:40); the silica in the residue is then removed by treatment with hydrofluoric acid. Trulot and Riley[1] have, however, shown that it is necessary to evaporate with sulphuric acid, and ignite, as otherwise titanium is volatilised as the fluoride $TiF_4.2HF$. The titanic acid is then dissolved by fusion with acid potassium sulphate, the melt dissolved in water, and the titanic acid precipitated by prolonged boiling. Any ferric iron present is reduced to the ferrous condition by passing sulphuretted hydrogen into the solution, whereby any precipitation of basic sulphate is prevented. When the ore contains more than 0·1 per cent. of phosphoric acid, the residue, after treatment with hydrofluoric acid, is fused with sodium carbonate, or the phosphoric acid is precipitated with the titanium. The aqueous solution then contains the whole of the phosphoric acid, whilst the titanic acid remains in the residue and is fused with acid potassium sulphate.

Tungsten.—Iron ores proper very seldom contain tungsten. From 1 to 2 g. of the finely divided sample is digested in hydrochloric acid with the addition of nitric acid from time to time. When decomposition is apparently complete, it is evaporated to dryness, hard baking being avoided. The residue is treated once more with hydrochloric acid and again taken to dryness. It is taken up with hydrochloric acid, diluted, filtered, and the residue washed. The tungstic acid is now dissolved in ammonia, and the solution obtained filtered, evaporated to dryness in a tared platinum dish, ignited and weighed. In case the tungstic acid is contaminated with silica, iron, etc., a few drops of hydrofluoric acid are added and the dish again ignited and weighed. The tungstic acid remaining is fused with sodium carbonate and extracted with water, any insoluble residue is filtered off, ignited, weighed, and deducted from the weight of tungstic acid obtained.

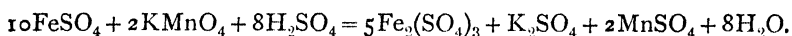
Carbon Dioxide.—If required, this may be determined by the loss of weight on treatment with acid in a Schrötter's or similar apparatus.

[1] *Stahl u. Eisen*, 1906, **26**, 88.

2. Volumetric Analysis

Iron.—The volumetric determination of iron is based on processes of reduction or oxidation by means of a standard solution. Iron ores never yield a wholly ferrous or wholly ferric solution in the ordinary way, so that titration must be preceded by complete oxidation or reduction according to the method adopted. The most important methods are:—Oxidation with potassium permanganate or bichromate and reduction with stannous chloride.

1. *Permanganate Method.* The decoloration of potassium permanganate by ferrous salts is a very sharp and delicate reaction; it takes place according to the following equation:—

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Iron, in the ferrous condition, can thus be determined by adding permanganate, until a faint pink colour becomes permanent. One c.c. of an exactly decinormal solution of potassium permanganate would correspond to 5·584 mg. of iron; in practice, a solution containing about 5 g. $KMnO_4$ per litre is made up. Permanganate solutions were formerly regarded as unstable, but it is now known that if they are boiled when made up, and then protected from light, they remain unchanged for months (*cf.* Vol. I., p. 59).

For the standardisation of the solution, iron wire may be used provided its content of iron is known exactly. Electrolytic iron also can now be obtained of a high degree of purity and is suitable for standardisation. Ferrous ammonium sulphate, which is easily obtainable in a pure state is a convenient salt for the standardisation as it contains almost exactly one-seventh of its weight of iron. Sodium oxalate is sometimes used as it can be obtained in the pure state and is not hygroscopic (*cf.* Vol. I., p. 61).

The determination of iron by means of permanganate is best carried out in solutions containing no acid other than sulphuric. Wherever possible, therefore, ores for assay should be dissolved in sulphuric acid; if this be not feasible, the sample is dissolved in hydrochloric acid and the solution evaporated with sulphuric acid. Carbonaceous ores, bog ores, etc., must previously be freed from organic matter by roasting. A solution of 0·5 to 1·0 g. of ore is prepared and the iron reduced to the ferrous condition by means of zinc (free from iron and carbon). The zinc may be wrapped round with platinum; reduction is complete when no coloration is produced with potassium thiocyanate. The solution is then made up to 100 c.c. with cold boiled water, and portions of 20 c.c. titrated.

Zinc dust, which has the advantage of acting almost instantaneously, is sometimes recommended as a reducing agent. When this is used the solution must not approach neutrality, or iron hydroxides may be

precipitated; on the other hand, any large excess of acid tends to retard the action of the zinc. It is always necessary to make a blank determination of iron in the zinc dust.

According to Carnegie,[1] the reduction is advantageously effected by covering the bottom of a narrow beaker with zinc dust, previously passed through a muslin bag, and a measured volume of the iron solution, nearly neutralised with ammonia, added; after vigorous stirring, a known volume of dilute sulphuric acid is introduced and the liquid again well stirred. An aliquot part of the clear solution is then withdrawn by means of a pipette provided with a filtering extension over the nozzle. C. Jones[2] recommends the use of a reducing tube consisting of a glass tube tied over at the bottom with muslin and charged with zinc dust which has passed a 40 to 60 mm. mesh sieve. An iron solution is fully reduced after being poured through once or oftener, and is then ready for titration; a specially designed tube may be employed, which holds 300 g. of zinc and serves for sixty reductions[3] (*cf.* p. 75).

The preparation of a purely sulphuric acid solution of iron ore is tedious, but hydrochloric acid solutions do not always lend themselves to titration with permanganate, since the acid may react with production of free chlorine. With a small excess of free acid, a very dilute solution and low temperature, the titration may be carried out without this secondary reaction; in any case, the formation of chlorine is easily detected by the smell. The danger is entirely obviated if a large excess of manganous salt is added.

A point greatly in favour of hydrochloric solutions is that they can be reduced with stannous chloride instead of with zinc. This method, as worked out by Reinhardt,[4] is as follows:—The solution of iron ore in hydrochloric acid is decolorised at boiling temperature by stannous chloride, and after cooling, 60 c.c. of an aqueous solution of mercuric chloride added to remove the excess of the reducing agent; the solution is diluted, and 60 c.c. of an acid solution of manganous sulphate added. The titration with permanganate then proceeds smoothly and accurately. Since the ferric chloride produced is apt to mask the end-reaction, it is well to add phosphoric acid, which yields colourless ferric phosphate. Reinhardt's solutions are made up in the following concentrations:—Potassium permanganate 6 g., mercuric chloride 50 g., and stannous chloride containing 30 g. of tin, per litre. The manganous sulphate solution is made up with 66·6 g. of manganous sulphate, 333·3 c.c. of phosphoric acid (sp. gr. 1·3) and 133 c.c. of strong sulphuric acid in the litre.

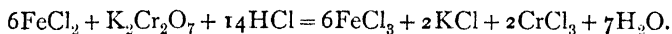
[1] *J. Chem. Soc.*, 1888, **53**, 468. [2] *Chem. News*, 1889, **60**, 93.

[3] *Z. anal. Chem.*, 1890, **29**, 59; *J. Amer. Chem. Soc.*, 1899, **21**, 723.

[4] *Stahl u. Eisen*, 1884, **4**, 704; 1889, **9**, 584; *J. Iron and Steel Inst.*, 1885, i., 299; 1889, i., 400; 1890, i., 375.

Experiments made to determine the influence of copper, arsenic, chromium, nickel, titanium, lead, and antimony on the determination of iron by this method have shown that only antimony has an appreciable influence on the results; as this metal is seldom found in iron ores, its influence is not regarded as important.[1]

2. *Bichromate Method.* Whereas the volumetric determination of iron with potassium permanganate necessitates special conditions in presence of hydrochloric acid, the volumetric determination of iron with potassium bichromate is free from this drawback. An external indicator is required in the titration, since the change from the yellow bichromate to the green chromic chloride solutions cannot be observed directly. The oxidation takes place according to the equation :—

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 6FeCl_3 + 2KCl + 2CrCl_3 + 7H_2O.$$

To carry out the determination, the ore is dissolved in hydrochloric acid, reduced with zinc or with stannous chloride, the excess of the latter removed with mercuric chloride, the solution diluted somewhat, rendered strongly acid with dilute sulphuric acid, and titrated in aliquot portions with potassium bichromate solution. A drop of the solution is taken out and mixed on a porcelain plate with a drop of very dilute potassium ferricyanide solution from time to time during the titration; a blue, and then a green, coloration is produced so long as any iron remains unoxidised; after the oxidation is complete, the colour will remain pure yellow. The approximate quantity of bichromate required is first determined by a preliminary titration; one or more further titrations are then made, the test for the completion of the reaction being made by adding the bichromate solution in quantities of 0·1 c.c. at a time.

The standard solution is quite permanent, and is made up by dissolving 4·9 g. of fused potassium bichromate in a litre of water. One c.c. of this solution is = 5·584 mg. Fe. The strength of the solution should be checked by means of a standard iron solution.

3. *Stannous Chloride Method.* For standardising, the iron or oxide of known value is dissolved in concentrated hydrochloric acid, carefully oxidised with potassium chlorate, the solution freed from chlorine by boiling, and made up to a definite volume, aliquot parts of which are titrated with the stannous chloride solution. To make up the latter, granulated tin is heated with concentrated hydrochloric acid until the evolution of hydrogen ceases, and the liquid diluted with nine volumes of hydrochloric acid (1 : 2). The strength of this solution can under no circumstances be regarded as constant, but rapid oxidation can be avoided by storing it in a bottle having a tap at the bottom and connected at the upper end with a supply of coal gas or hydrogen. The

[1] Cf. *Stahl u. Eisen*, 1908, **28**, 508; *J. Iron and Steel Inst.*, 1908, iii., 673.

titration is carried out at boiling temperature, in presence of a considerable excess of hydrochloric acid. The reaction is as follows:—

$$2FeCl_3 + SnCl_2 = SnCl_4 + 2FeCl_2.$$

With practice it is quite easy to titrate from the yellow ferric solution to the colourless ferrous solution without further aids, but the reaction slows down somewhat towards the end, so that time must be allowed for the stannous chloride to react. An alternative and safer method is to add stannous chloride in slight excess, cool, dilute, add starch paste and titrate back with standard iodine solution. The latter is made up by dissolving about 10 g. of iodine in potassium iodide solution and diluting to 1 litre, and is standardised against the solution of stannous chloride.

For the actual determination, from 2·5 to 5·0 g. of the ore is dissolved as above, the solution made up to 100 c.c., and 20 c.c. (=0·5 to 1·0 g. of ore) taken for the titration. A preliminary titration is first made, to ascertain about how much stannous chloride is required for the reduction; in the final titration the bulk of the stannous chloride solution is added at once, and the estimation completed by the subsequent addition of small portions at a time.

The titration can also be effected by using sodium molybdate as an external indicator;[1] a minute excess of stannous chloride reduces the molybdate and gives a blue coloration.

4. *Iodine Method.*—Iron when present entirely in the ferric condition may be determined by the addition of potassium iodide to the faintly acid solution and titrating the iodine liberated in the usual way with thiosulphate.[2] This method is frequently useful in determining small quantities of iron rapidly.

5. *Electrometric Titration.*—During recent years the application of electrometric titration methods to routine analyses has received much attention. These methods are based on the application of the hydrogen electrode, and their value depends on the fact that if two electrodes of the same metal are placed in solutions containing the ion of the metal in different concentrations and these solutions are placed in electrical contact, either through a porous partition or by means of a siphon, or even separated by gravity alone, there will exist between the two electrodes a difference of potential, the determination of which makes it possible to detect quite accurately even very small ionic concentrations. If, instead of a hydrogen electrode, an unattackable electrode be used, it is possible to determine the end point of oxidation and reduction reactions such as those used in the determination of

[1] *Cf.* Zengelis, *Ber.*, 1901, **34**, 2046; *J. Soc. Chem. Ind.*, 1901, **20**, 840.
[2] I. W. Wark, *J. Chem. Soc.* 1922, **121**, 358.

iron.[1] Convenient forms of apparatus for carrying out electrometric titrations have been put on the market by the Arthur H. Thomas Company, Philadelphia, A. Gallenkamp and Co., Ltd., London, and the Central Scientific Company, Chicago.

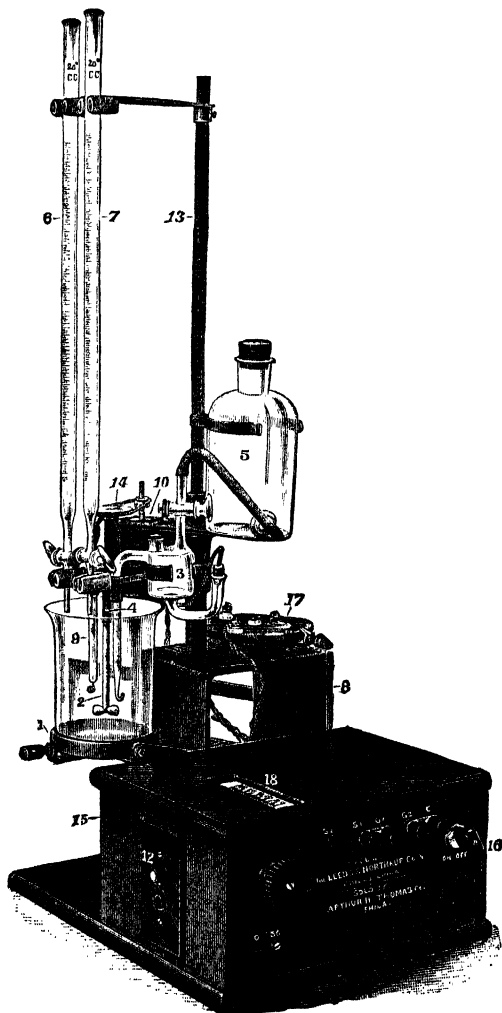



Fig. 8.

The apparatus shown in Fig. 3 is known as the Kelley apparatus,[2] and is supplied by the first mentioned company. This apparatus consists essentially of a wooden case containing two dry cells, an

[1] *Cf.* G. S. Forbes and E. P. Bartlett, *J. Amer. Chem. Soc.* 1913, 35, 1527; J. C. Hostetter and H. S. Roberts, *J. Amer. Chem. Soc.*, 1919, 41, 1337; G. L. Kelley and R. T. Bohn, *J. Amer. Chem. Soc.*, 1919, 41, 1776.

[2] *Ind. Eng. Chem.* 1917, 9, 780.

adjustable resistance and a reflecting galvanometer. On the upper surface of the case is a ground glass scale on which the galvanometer readings are taken. Milled heads are provided for adjusting the zero point of the galvanometer and for controlling the switches for the galvanometer light and motor. Attached to the same stand as the wooden case is an upright standard (13) arranged to carry the burettes (6, 7), electrodes (3, 9), and the motor (10), and also a reservoir for the electrolyte. An adjustable support is provided for the beaker in which the titrations are made. Before using the apparatus, the glass tube of the platinum electrode (9) is filled with mercury for making contact. The calomel cell is also filled to a depth of about a quarter of an inch with mercury, allowing it to rise to the same height in the tube connected to the bottom of the cell. A thin layer of calomel is then placed over the mercury and the cell is filled with a normal solution of potassium chloride, which has been shaken with freshly precipitated calomel and the liquid allowed to settle. In using the instrument, the solution to be titrated is placed in the beaker which is then raised and locked in position so that the stirrer (2) is below the liquid. The switch (12) controlling the galvanometer light and motor is then closed and the potentiometer circuit is also closed by means of the switch (16), and the beam of light is brought on to the scale by an adjustment of the resistance. During the titration the beam of light is carefully watched until a large movement accompanied by a permanent change of potential is obtained, which indicates the end point.

Two burettes are used, one for the reducing agent such as stannous chloride, ferrous ammonium sulphate, etc., and the other for the oxidising agent such as potassium bichromate, potassium permanganate, etc. The end point may be obtained by simple observation, but the results of titrations may also be plotted in curves, the E.M.F. readings being plotted as ordinates and c.c.'s of reacting solution as abscissæ.

The chief advantages obtained by this method of analysis are rapidity and the non-interference of deep colours and turbidity in the solutions. A keen perception of change in colour is also unnecessary in the use of this method.

For the determination of iron, permanganate or bichromate solutions may be used, or to titrate ferric iron solutions, stannous chloride may be used.

Permanganate titrations are in themselves so convenient and the end-point so well marked that the electrometric method of determining the end-point has little advantage. With large quantities of ferric iron present, however, the appearance of the pink colour is frequently masked so that too much permanganate is added, an error which is avoided in the electrometric method.

For bichromate titrations, the usual method is followed for the preparation of the solution in the ferrous condition, which is then titrated with the bichromate solution of appropriate strength. During the titration, slight changes of voltage will occur, and as the end-point is reached the light on the scale will show a growing instability, until at the end-point there will be a considerable and permanent change indicating a considerable change in voltage. If the end-point is passed, the original voltage may be obtained again by the addition of a known volume of some standard reducing agent, such as ferrous ammonium sulphate, and the end-point redetermined.

The end-point is detected more accurately by this method than by spotting-out with potassium ferricyanide solution.

Stannous chloride solution may be used for the determination of iron in solution in the ferric condition. In this reaction the fall of potential at the end-point is clearly marked, the voltage falling to below zero, that is, becoming actually negative.

The electrometric method of titration may also be used for the determination of the amounts of ferric and ferrous iron in one solution.[1] The solution is first titrated with stannous chloride solution and the amount required to produce the marked fall of potential noted above will be equivalent to the amount of ferric iron present. A slight excess of stannous chloride is then added and the titration continued with standard bichromate solution. The first marked increase in voltage corresponds to the oxidation of the excess stannous chloride just added, and is the point at which the second part of the titration, that is for the determination of the total iron present, begins. The volume of bichromate required to pass from this point to the second sharp increase in voltage, is the volume required to oxidise all the iron present from ferrous to ferric condition and is therefore equivalent to the total iron. By deducting the amount of iron in the ferric condition obtained by the stannous chloride titration, the amount of iron originally present as ferrous iron is obtained.

The solution must be made up so as to avoid any oxidation through contact with air. For this purpose the method proposed by Jahoda[2] for dissolving standard iron wire may be adopted. The ore is placed, together with a pinch of sodium bicarbonate, in the flask *a* (Fig. 4), acid poured in, and a cork fitted with a glass tube bent twice at right angles inserted. The open end of the latter dips into a beaker, *b*, containing a dilute solution of sodium bicarbonate. When solution is complete and the flask is allowed to cool, some of the bicarbonate sucks back, but is prevented from filling the flask owing to the evolution of carbon dioxide; this is repeated as the cooling proceeds, so that a

[1] *Cf.* Hostetter and Roberts, *J. Amer. Chem. Soc.*, 1919, 41, 1337.

[2] *Z. angew. Chem.*, 1889, 2, 87.

solution of ore in an atmosphere of pure carbon dioxide is finally obtained. The Contat-Göckel bulb (see Vol. I., p. 63) acts on the same principle and is much more compact.

When iron is present in an ore in both states of oxidation, there is no difficulty in determining firstly the ferrous iron and secondly the ferric iron by the permanganate or bichromate titrations. This can be done on one and the same portion of the sample, or on separate portions.

Manganese.—The most commonly used volumetric methods for manganese are based on the following reaction, which was first applied by Guyard[1]:—

$$3MnO + Mn_2O_7 = 5MnO_2.$$

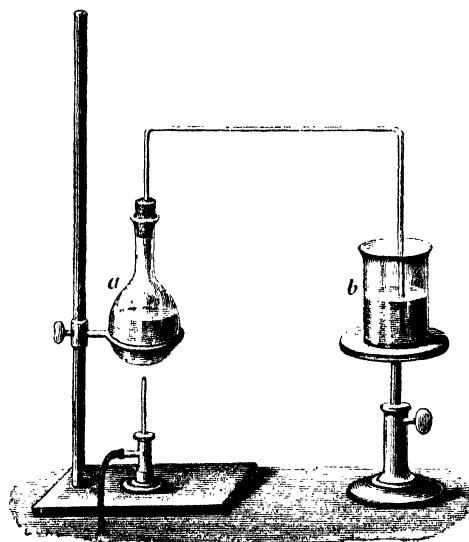
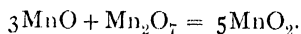



Fig. 4.

Owing to its acidic nature, manganese dioxide tends to form compounds with manganous oxide, such as $MnO.5MnO_2$; consequently the above reaction never quite holds good, and the value of a standard solution cannot be deduced from its content of permanganate, but must be ascertained empirically.

According to some methods, the manganese is first separated as dioxide, this reduced to a manganous salt, and titrated with permanganate. In others, iron is removed and the filtrate titrated directly, either with or without adding an excess and titrating back. The following method is that of Volhard,[2] modified by N. Wolff.[3]

[1] *Chem. News*, 1863, **8**, 292.
[2] *Annalen*, 1879, **198**, 318; *Chem. News*, 1879, **40**, 207; *J. Iron and Steel Inst.*, 1880, i., 355.
[3] *Stahl u. Eisen*, 1884, **4**, 702; *J. Iron and Steel Inst.*, 1885, i., 301; *Stahl u. Eisen*, 1890, **11**, 377.

In this method all the manganese must be present as manganous chloride and all the iron as ferric chloride. The iron is precipitated by means of zinc oxide and the manganese titrated with standard permanganate without filtering, at a temperature of 80°. A little acetic acid sharpens the end point.

The permanganate solution is made up by dissolving 9 g. in 1000 c.c. Its value may be determined by reducing, say, 30 c.c. of the solution itself to manganous chloride by means of hydrochloric acid, neutralising with zinc oxide, and titrating at 80°. As the result of numerous investigations, carried out independently and with solutions of different concentrations, it was found that 100 c.c. of the reduced solution require 66 c.c. for titration, as against 66·66 c.c. calculated from the equation given above. When the exact permanganate content of a solution has been determined by means of sodium oxalate, its value for the estimation of manganese is thus ascertained. While this correction is still fairly generally accepted, investigations by De Koninck[1] indicate that the reaction does proceed exactly in accordance with the equation given above; the factor 0·2952 for the conversion of the iron-value of the permanganate solution to the value for manganese is therefore applicable.

To carry out the determination in ores and slags, which leave a residue free from manganese on treatment with hydrochloric acid, 1 g. is weighed out for ores containing up to 20 per cent. of manganese, and 0·5 g. for those containing 20 to 50 per cent. The sample is weighed into a litre conical flask, digested with 20 c.c. of hydrochloric acid (sp. gr. 1·19), and boiled with the addition of 3 g. of potassium chlorate, until all chlorine is expelled. Ores not answering to this description are evaporated in a covered porcelain dish with hydrochloric acid and a little chlorate until the separated silica has become granular, the residue digested with hydrochloric acid and filtered. The residue from the filtration is then fused with mixed carbonates, and the melt subjected to the same treatment as the original material. The combined filtrates should be evaporated to 100 c.c. if necessary. Three samples should always be dissolved, and the solutions finally collected in litre conical flasks.

When the substance contains little iron and much phosphorus or arsenic (*e.g.*, basic slags), sufficient iron must be added to ensure the precipitation of all the phosphoric and arsenic acids. The iron is added in the form of manganese-free oxide or chloride. The solutions are tested for ferrous iron with potassium ferricyanide, and, if necessary, oxidised with hydrogen peroxide; they are then boiled so as to obtain all the manganese in the manganous condition. The iron is precipitated with pure ignited zinc oxide suspended in water, which is added in

[1] *Bull. Soc. Chim. Belg.*, 1904, **18**, 56; *Chem. Centr.*, 1904, I., 1429.

small portions at a time, with thorough agitation, until all the iron is precipitated; the end-point is indicated by the sudden coagulation of the ferric hydroxide. At this stage the supernatant liquid will still have a brownish colour, but will, as a rule, clear to a colourless solution on shaking; until this condition is attained, further small quantities of zinc oxide are added, if required, and the liquid heated. The precipitate must not contain much zinc, and must show the brown colour of ferric hydroxide; a considerable excess of zinc oxide leads to low results. Any milkiness due to zinc oxide affects the end-reaction, and should be removed by the cautious addition of dilute hydrochloric acid. The liquid is then diluted to 400 c.c. (which is taken as the uniform volume for all titrations), heated to 80°, and standard permanganate added until a red coloration persists on shaking, in order to obtain an approximate figure for the amount required. Suppose 23 c.c. is required. The solution from the second sample is similarly precipitated and titrated

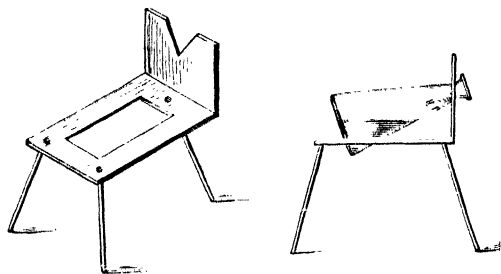



Fig. 5.

by adding 22 c.c. of permanganate and completing the titration with 0·2 c.c. at a time, until a red tint is attained equal to that produced by 0·1 c.c. of permanganate in 400 c.c. of water. It is well to have a flask of water thus coloured at hand; the tints are never quite the same, but can be equalised sufficiently for practical purposes. If, for example, 22·6 c.c. is required to reach this end-point, the value 22·5 c.c. is used in calculating the result. The third quantity may be titrated as a check.

After each addition of the standard solution, the flask is well shaken and the contents allowed to settle sufficiently to show the colour of the supernatant liquid. This is facilitated by the use of the special stand shown in Fig. 5.

The three separate determinations, as described above, are only necessary if the manganese content is unknown; if the quantity is known approximately, two determinations will suffice. When carried out as above, the method is fairly rapid.

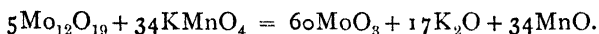
The majority of other metals likely to occur in iron ores do not affect the accuracy of this method appreciably, as they are usually present only in small quantities. Copper is completely precipitated as

hydroxide by the zinc oxide. Nickel and lead are apt to cause high results when present in considerable quantity; cobalt and chromium, however, have this effect even when present in very small amounts. In order to remove cobalt, nickel, and lead, the hydrochloric acid solution of the ore is treated with an excess of ammonia and ammonium sulphide, and then rendered slightly acid with hydrochloric acid; after filtering, boiling, and oxidising with potassium chlorate, the solution is ready for the determination of the manganese. When chromium is present, it is best to precipitate all the manganese by the chlorate method (p. 53), dissolve the washed peroxide in hydrochloric acid, boil, neutralise with zinc oxide, and titrate. Tungsten is oxidised to tungstic acid, and remains in the residue on filtration.

Low[1] dissolves 0·5 g. of ore in 10 c.c. of hydrochloric acid or aqua regia, evaporates nearly to dryness, adds 75 c.c. of hot water and excess of zinc oxide, boils, and treats with 25 to 50 c.c. of bromine water, according to the proportion of manganese present. The excess of bromine is boiled off, the precipitate filtered, washed, returned to the beaker, and dissolved in 50 c.c. of dilute sulphuric acid (1 : 9) with the aid of a known volume of oxalic acid or of ferrous ammonium sulphate solution. After dilution the excess of the latter is titrated back with permanganate.

Probably the most generally useful volumetric process for determining manganese is the bismuthate method. The ore is dissolved in hydrochloric acid, using a little hydrofluoric acid if necessary to ensure that no manganese remains in the insoluble residue. The hydrochloric and hydrofluoric acids are then completely removed by evaporating with sulphuric acid till fuming. The mass is dissolved in nitric acid of specific gravity 1·20 and the solution, or an aliquot part of it, treated in the same way as described for steels (p. 56).

Phosphorus.—According to Emmerton's method, described fully by Blair,[2] phosphorus may be determined volumetrically in the phospho-molybdate precipitate by means of permanganate, according to the following reaction:—

$$5Mo_{12}O_{19} + 34KMnO_4 = 60MoO_3 + 17K_2O + 34MnO.$$

The strength of the permanganate, in terms of iron, is multiplied by 0·01651 to give the phosphorus, or by 0·03781 to give phosphoric anhydride.

To carry out the determination, the yellow precipitate is thoroughly washed, the filter paper pierced, the precipitate washed off and dissolved in dilute ammonia (1 : 4) in a 1000 c.c. flask; a large excess of ammonia should be avoided. Ten grams of granulated zinc and 800 c.c. of warm

[1] *J. Anal. and Applied Chem.*, 1892, **6**, 663; *Chem. News*, 1893, **67**, 162.
[2] *The Chemical Analysis of Iron*, p. 92.

dilute sulphuric acid (1 : 4) are then added and the flask warmed for ten minutes, without boiling. A change of colour is observed as the molybdic acid is reduced to the oxide, $Mo_{12}O_{19}$, the final tint being a dark olive green. The liquid is poured through a large pleated filter, the residue washed by decantation once with cold water, and the washings poured through the filter paper. The filtrate assumes a yellow colour, owing to the action of the air, but is not appreciably oxidised; it is then titrated with permanganate; shortly before complete oxidation it becomes colourless, so that the change to pink is observed without difficulty.

Phosphorus may also be determined volumetrically[1] by dissolving the well-washed yellow molybdate precipitate in *N*/10 sodium hydroxide solution, and titrating the excess with *N*/10 nitric acid, phenolphthalein being used as an indicator. Each c.c. of *N*/10 sodium hydroxide is equivalent to 0·000129 g. phosphorus.

Sulphur.—The following method, originally due to Watson[2] and modified by Lunge,[3] for the determination of sulphur in pyrites cinders is applicable (*cf.* Vol. I., pp. 367-9). About 3·2 g. of substance is mixed with exactly 2 g. of sodium bicarbonate, the alkalinity of which has been determined by titration. The mixture is heated in a 20 c.c. nickel crucible, at first quite gently for ten to fifteen minutes, so that the tip of the flame just touches the bottom of the crucible, then to a full red heat for twenty minutes. The mass must not be allowed to fuse. To avoid mechanical loss, the crucible is kept covered and the contents are not stirred during the preliminary heating, but are stirred frequently with a platinum or nickel rod during the ignition at the higher temperature. After cooling, the mass, which should be black and quite porous, is transferred to a porcelain dish and lixiviated with boiling water. If, as sometimes happens, the solution filters with difficulty, it is advisable to add a concentrated solution of sodium chloride accurately neutralised with hydrochloric acid in presence of methyl orange, to moisten the filter paper with the same solution, and to agitate the liquid in the filter during filtration. After repeating the extraction several times and washing with sodium chloride solution, the clear united filtrates are titrated back with *N*/5 hydrochloric acid and methyl orange.

Chromium.—A solution containing all the chromium as sodium or ammonium chromate is prepared as in the gravimetric method described on p. 12. After filtering and making up to 250 c.c., an aliquot part is taken, a known quantity of ferrous ammonium sulphate added and the excess titrated with bichromate or permanganate solution (see Steel Analysis, p. 72).

[1] Handy, *Chem. News*, 1897, **76**, 324.
[2] *J. Soc. Chem. Ind.*, 1888, **7**, 305.
[3] *Z. angew. Chem.*, 1892, **5**, 447; *J. Soc. Chem. Ind.*, 1893, **12**, 292.

Vanadium.—A small proportion of vanadium occurs in a variety of iron ores. For its determination 10 to 12 g. of the ore is dissolved in hydrochloric acid, any contained ferrous iron oxidised with nitric acid, an excess of which should be avoided, the solution filtered, and the filtrate treated as described on p. 77.

3. Analysis of Fluxes and Slags

Fluxes.—These are analysed by methods similar to those described for the analysis of iron ores. Limestone is by far the commonest flux used and it is generally analysed for insoluble siliceous residue, lime, magnesia, phosphorus, and sulphur. When required for making calculations for blast furnace charges, as it is necessary to know the amount of silica and alumina present, the insoluble siliceous residue must be decomposed and the silica, alumina, lime, and magnesia present determined.

For the analysis, 1 g. of the sample is dissolved in 5 c.c. of hydrochloric acid diluted with 25 c.c. of water to which a little bromine water has been added. It is digested until all action ceases and then evaporated to dryness. The residue is re-treated with dilute hydrochloric acid, filtered, washed with hot water, dried, ignited and weighed as insoluble residue. This residue is fused with sodium carbonate, the fused mass dissolved in hot water, acidified with hydrochloric acid and evaporated to dryness; it is again evaporated to dryness with hydrochloric acid, baked, and then taken up with the same acid and filtered. The insoluble silica is ignited and weighed as such, and the filtrate is added to the main filtrate obtained from the insoluble residue.

The iron and alumina are precipitated in the filtrate by means of ammonia, a large excess being avoided, the lime is precipitated as oxalate by means of ammonium oxalate, and the magnesia is precipitated in the filtrate from this by means of sodium ammonium phosphate (*cf.* Vol. I. pp. 510-13).

To determine sulphur, 1 g. is fused with sodium carbonate and potassium nitrate as described for the determination of sulphur in iron ores (p. 19).

For the determination of phosphorus, 20 g. is dissolved in dilute hydrochloric acid, the insoluble residue is filtered off and ignited, a little hydrofluoric acid and a few drops of sulphuric acid are added and evaporated to dryness, the mass fused with sodium carbonate, digested with water, filtered, acidified with hydrochloric acid, and the solution added to the main filtrate. To this solution a few c.c. of ferric chloride solution are added, then ammonia until the solution is slightly alkaline to litmus, and then acetic acid until decidedly acid; it is boiled for a few minutes, filtered, and the precipitate washed with hot water.

This precipitate is dissolved in dilute hydrochloric acid, evaporated to dryness, taken up with dilute nitric acid and the determination of phosphorus proceeded with as described on p. 16.

Slags.—The analysis of slags does not necessitate any exceptional treatment. Highly ferruginous refinery slags behave like difficultly soluble ores. Basic slags owe their value to a high content of phosphorus, and are often assayed for this constituent alone, the method given on p. 17 being carried out on small quantities of material.

Full analyses of blast furnace slag are frequently required, and are carried out like any other silicate analysis, except that alkali fusion is often unnecessary. The slag contains a certain amount of sulphur as barium, calcium, and manganese sulphides, and this is determined by the sulphuretted hydrogen method (p. 57).

The shortened method of analysis of blast furnace slag, described by Textor,[1] is not quite accurate, but suffices for most purposes. Three samples of the finely ground slag are weighed out: No. 1, of 1·325 g., for the determination of lime and magnesia; No. 2, of 0·5 g., for silica and alumina; and No. 3, also of 0·5 g., for sulphur. Nos. 1 and 2 are each stirred up with 25 c.c. of boiling water, together with 25 c.c. and 10 c.c. respectively of hydrochloric acid (1 : 1), and boiled, with continual agitation, until dissolved. No. 2 is oxidised with a little nitric acid, evaporated to dryness, and heated to drive off hydrochloric acid. No. 1 is similarly oxidised, diluted to 300 or 350 c.c., treated with 25 c.c. of strong ammonia (which is added very gradually, to avoid precipitation of magnesia), and made up to 530 c.c. Two hundred and fifty c.c. of the filtrate, corresponding to 0·625 g. of slag, is taken for the determination of magnesia, and 200 c.c., corresponding to 0·5 g., for that of lime. Both portions are boiled with 25 c.c. of ammonium oxalate solution; the portion for the magnesia estimation is then cooled and made up to 300 c.c., whilst that for the determination of the lime is filtered, the precipitate washed, dissolved in sulphuric acid, and titrated with potassium permanganate. Of the diluted magnesia portion, 240 c.c., corresponding to 0·5 g. of slag, are filtered off, and poured into 10 c.c. of sodium phosphate solution and 10 c.c. of strong ammonia contained in a beaker; precipitation is aided by blowing air through the liquid for ten minutes. Meanwhile all the silica in sample No. 2 will have been rendered insoluble. The residue is digested with 15 c.c. of concentrated hydrochloric acid. During this time the ammonium magnesium phosphate, precipitated as above, is filtered off, washed, ignited, and weighed as magnesium pyrophosphate with the usual precautions. The residue from No. 2 is then taken up with hot water, boiled, and filtered, and the silica washed, ignited, and

[1] *J. Anal. and Applied Chem.*, 1893, 7, 257; *J. Iron and Steel Inst.*, 1893, ii., 539; 1894, ii., 498.

weighed. Alumina is precipitated in the filtrate with ammonia. Iron is usually included with the alumina, but if it is present in considerable quantity, a separate sample of the slag is used and the iron determined volumetrically. Manganese, if present, will, for the most part, go into the magnesia precipitate; the method is not applicable to the more manganiferous kinds of slag. Finally, sulphur is determined in sample No. 3, by suspending it in 150 c.c. of hot water, adding starch solution and 15 c.c. of standard iodine solution (1 c.c. = 0·1 per cent. of sulphur), then 30 c.c. of concentrated hydrochloric acid, and titrating back the excess of iodine with thiosulphate solution.

4. Dry Assays

The dry assays at one time in use in the iron industry are far less accurate than the wet ones, and are, therefore, deservedly obsolete. One or two dry tests, however, are still in use for iron ores. The so-called German assay, for instance, aims at reproducing the effects of blast furnace smelting. The ore is ignited, with the requisite admixtures, in a carbon-lined crucible, and the resulting metal is detached and weighed. The mixing should be exactly the same as for a blast furnace charge, and be based upon a previous analysis of the ore. In this way the approximate yield of pig iron is ascertained and information is gained as to the behaviour of the ore in smelting. Details of the method are given in the handbooks of Balling,[1] Kerl, and others. A second dry test is the reducibility test, which has for its object the determination of the behaviour of an ore towards reducing agents. A method has been worked out by Wiborgh[2] by means of which this property may be determined quantitatively.

Ores which are reduced by carbon monoxide are considered easily reducible, whilst those which are reducible only by carbon are classed as difficult to reduce. The degree of reducibility depends on the content of oxygen and on the density of the ore, and is roughly proportional directly to the former and inversely to the latter.

II.—ANALYSIS OF IRON AND STEEL

Nearly all varieties of commercial iron and steel contain carbon, silicon, and manganese as normal constituents. They also contain sulphur, phosphorus, copper, arsenic, and sometimes titanium by way of impurities. Traces of nitrogen, oxygen, etc., are often present, but they occur in such minute quantities as not to influence the properties

[1] C. M. Balling, *Die Probierkunde*, 1879.
[2] *Stahl u. Eisen*, 1897, 17, 804; *Chem. News*, 1898, 78, 4.

of the metal perceptibly, and are therefore seldom determined. The determination of chromium, tungsten, nickel, cobalt, vanadium, molybdenum, and titanium is frequently of importance, since these metals occur as essential components of certain steels and of the alloys employed in making them. In the examination of galvanised iron and tin plate, zinc and tin may have to be determined and in other cases, aluminium, boron, zirconium, tantalum, and cerium may be present. Under special conditions it may be necessary to extract and examine the occluded gases present or to determine the amount of oxide and slag inclusions. As a rule, the constituents of an iron or steel are known beforehand, so that qualitative analysis is generally superfluous. It may happen, however, that one or more of the rarer constituents has to be tested for.

Sampling.—The taking of samples of wrought iron or of grey cast iron for analysis is a comparatively simple matter. The metal is best comminuted by drilling, planing, or turning, to the degree of fineness required. White cast iron and the hardest kinds of steel may be dealt with by means of tools made of special steels; when, as often happens, such tools are not at hand, and also when sampling ferro-manganese, ferro-chrome, ferro-silicon, etc., pieces should be chipped off the metal with a large hammer and then pounded in a specially hardened steel mortar. The fragments are sifted through a sieve of ½ mm. mesh and the residue again pounded up; this is repeated until the whole has passed through the sieve. Cast irons are never quite homogeneous, and the pig or casting should be sampled at several points, the outside portion being discarded.

A special difficulty arises in sampling grey cast iron, from which, on drilling, grains of graphite are detached and tend to segregate themselves from the specifically heavier iron. This may lead to errors in the carbon determinations up to 0·2 per cent. One remedy consists in sifting off the graphite and weighing out fine and coarse samples separately, in the original proportions, for each determination. It is difficult to obtain an absolutely representative sample of grey cast iron, but this is only a serious disadvantage in the determination of carbon.

In taking samples of steels, it is necessary to bear in mind that the material is never absolutely homogeneous and that during the solidification of the original ingots, segregation of carbon, phosphorus, etc., is most marked in the central upper portions. In forgings, castings, etc., the best position from which to obtain drillings is, in general, midway between the outside and the centre of the piece to be sampled, and care should be taken to discard the first drillings obtained from the outside skin.

In the sampling of hard tool steels, springs, etc., it is desirable to anneal these first by heating to a bright red heat and allowing to cool

slowly, precautions being taken to avoid oxidation. In the case of self-hardening and high-speed steels, prolonged annealing is necessary; the samples should be packed with lime in crucibles, heated in a muffle furnace, and cooled down slowly over a number of hours.

Carbon.—Carbon occurs in iron and steel in four modifications. Two of these—*graphite*, which is crystalline and rarely found in steels, but is a normal constituent of cast iron, and *temper-carbon*, which is amorphous and behaves like graphite, in that it is not acted upon by boiling hydrochloric or nitric acid—are present in mechanical admixture with the metal. *Carbide-carbon* is present in definite chemical combination as a carbide of iron or of one of the other metals present; whilst the fourth modification, *hardening carbon*, is present in steel as a solid solution of carbon or carbide in the metal.

Total Carbon.—There are numerous methods for determining total carbon, but in almost all cases the carbon is ultimately weighed as carbon dioxide. The procedure may consist in oxidising the metal directly by combustion in the dry or in the wet way, or in previously removing the iron by solution or volatilisation and then determining carbon in the residue by combustion.

1. *Direct Dry Combustion Method.* The oxidising medium may be either free oxygen alone, or free oxygen in conjunction with oxidising admixtures such as chlorates, chromates, or metallic oxides such as cupric oxide, or else inert agents such as alumina, magnesia, etc. For pig and cast irons, ignited manganese dioxide is a suitable admixture, while red lead or lead chromate is preferable for ferro-alloys.

The metal, in the form of either small shavings or drillings, is placed, with or without admixtures, in a platinum, nickel, clay, or porcelain boat, and introduced into a heated silica or porcelain tube the front end of which may be charged with copper oxide. The tubes may be heated, either in a suitable gas muffle, preferably one in which the flame does not come in direct contact with the tubes, or electrically. Furnaces are now available in which the heating units consist of opaque silica tubes wound with nichrome resistance wire, and packed round with insulating material. The combustion tubes are inserted into the furnace tubes and can be heated without risk of cracking. Suitable apparatus for purifying and drying the oxygen is attached to the inlet side of the tube, as shown in Fig. 6, and the other end is connected with a series of cooling and drying-tubes, the apparatus for absorbing the evolved carbon dioxide, and a final guard-tube containing hygroscopic material. The usual arrangement comprises first a tube containing a saturated solution of chromic acid in 50 per cent. sulphuric acid to absorb sulphur dioxide, then two drying-tubes, the first charged with concentrated sulphuric acid and

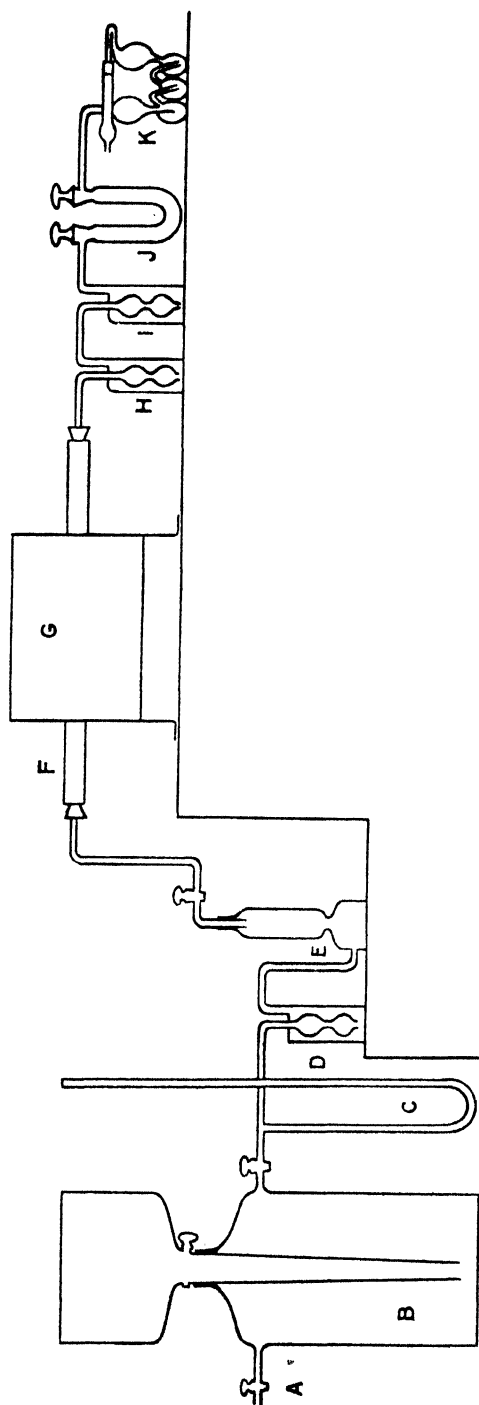



FIG. 6.—Apparatus for Determination of Carbon by Direct Dry Combustion.

A From oxygen cylinder.
B Gas-holder or other large reservoir.
C Pressure gauge.
D Arnold bulb containing caustic potash solution.
E Tower for solid caustic potash.
F Silica combustion tube.
G Electric tube furnace.
H Arnold bulb with sulphuric-chromic acid mixture.
I Arnold bulb with concentrated sulphuric acid.
J Calcium chloride U-tube.
K Potash bulb with calcium chloride tube.

the second with calcium chloride, followed by the absorption tubes filled with 50 per cent. potash solution or with soda lime and calcium chloride. A very efficient absorbent is ascarite (asbestos impregnated with sodium hydroxide), used in stoppered U-tubes. All the connections having been made secure, the combustion tube is heated to a bright red heat, the boat containing the sample is introduced, and a current of oxygen passed through. The regulation of the temperature requires care, since a certain minimum temperature, 950° to 1000° C., is necessary for reasonably rapid combustion of the carbon, while over-heating leads to the formation of molten ferroso-ferric oxide, which may cover the particles of iron, and thus prevent their oxidation. When the steel begins to burn oxygen is rapidly absorbed, and unless a large gas-holder is provided between the cylinder and the furnace, careful regulation of the flow is requisite in order to avoid great variations of pressure. According to Schneider,[1] the process is greatly facilitated and requires only moderate temperatures, if 3 g. of the iron is mixed with 10 g. of certain metallic powders (*e.g.*, three parts of lead to one of copper), or with the same quantity of powdered phosphor-copper. A better method of assisting oxidation is the addition of a known weight of a low carbon steel, the carbon in which has been previously determined and can be allowed for. The absorption tube is weighed before and after the combustion and the carbon calculated from the increase in weight due to the absorption of carbon dioxide.

A modification of this method, which permits of very rapid working given suitable apparatus, is described by Cain and Maxwell.[2] The weighed quantity of steel, with or without admixture, is transferred to a boat which has been previously heated in the combustion tube for a few minutes, the boat is replaced in position and the tube closed without delay. A rapid stream of oxygen is turned on and the products of combustion passed for about seven minutes through baryta solution, contained in a special form of absorption tube. The precipitated barium carbonate is filtered and washed with the aid of a filter pump, dissolved in a measured excess of standard hydrochloric acid, and the excess titrated with alkali.

J. Musatti and M. Croce[3] pass the products of combustion through a standard solution of barium hydroxide, and determine the residual hydroxide by titration with a standard solution of hydrochloric acid, using phenolphthalein as an indicator. Twelve to fifteen minutes are occupied by a determination.

[1] *Oesterr. Chem. Zeit.*, **42**, 241 ; *J. Iron and Steel Inst.*, 1894, ii., 488.

[2] *Ind. Eng. Chem.*, 1918, **10**, 520 ; *Analyst*, 1918, **43**, 359 ; *cf.* W. Brady, *Ind. Eng. Chem.*, 1914, **6**, 843.

[3] *Giorn. Chim. Ind. Appl.*, 1923, **5**, 217 ; *J. Iron and Steel Inst.*, 1923, ii., 484.

By the use of an absorbent consisting of a mixture of sodium hydroxide and asbestos, Stetser and Norton[1] claim to have reduced the time requisite for a combustion to about six minutes.

Direct dry combustion is a process requiring considerable experience, but is generally applicable to all classes of iron and steel which can be obtained in a sufficiently fine state of division, and is particularly applicable to ferro-alloys and alloy steels which are difficult to decompose with acids.

2. *Direct Wet Combustion Method.* The iron is oxidised by boiling with a mixture of chromic and sulphuric acids (v. Jüptner[2] and Gmelin[3]); the evolved gases may be further oxidised by dry combustion (Särnström). It is applicable to all kinds of iron and iron

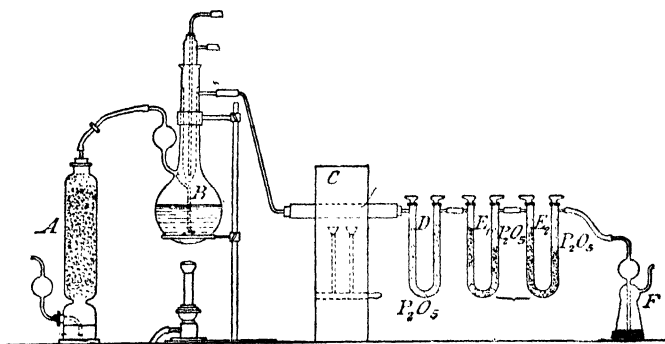



FIG. 7.

alloys except ferro-silicon and ferro-chrome. The following standard procedure was worked out by Corleis.[4]

The apparatus (Fig. 7) consists of a purifying cylinder A, a boiling flask B, a combustion tube C, packed with copper oxide, and three U-tubes. The first of these, D, is a drying tube, and is charged with phosphorus pentoxide; the two others, E_1 and E_2, serve for the quantitative absorption of the carbon dioxide, and contain soda-lime, with a short layer of phosphorus pentoxide at the exit end. The series is terminated by a small wash-bottle F, containing sulphuric acid, which serves both to prevent access of moist air to E and to show the rate of passage of the gases through the apparatus. The soda-lime tubes should have hollow ground-in stoppers; for the phosphoric oxide, plain U-tubes, sealed off at the upper ends, are

[1] *Iron Age*, 1918, **102**, 443.
[2] *Oesterr. Chem. Zeit.*, 1883, p. 493; *J. Iron and Steel Inst.*, 1883, ii., 779.
[3] *Oesterr. Chem. Zeit.*, **32**, 707; *J. Iron and Steel Inst.*, 1885, i., 246.
[4] *Stahl u. Eisen*, 1894, **14**, 587.

preferable. In order to save phosphoric oxide, the introduction of a sulphuric acid absorption vessel between C and D is sometimes adopted.

The most important part of the apparatus is the flask B, of which details and measurements are given in Fig. 8. A condenser *a* is ground into the neck *b* of the flask, which is widened out at *c* so as to provide a water-lute. A tube, reaching nearly to the bottom, is fused into the side of the flask; this is fitted with a bulb, as a safeguard against sucking back, and with a stoppered thistle funnel for introducing the liquid reagents; it must not be less than 6 mm. in bore, since it has a tendency to be blocked up with solid matter. The charge of metal is introduced into the flask either by means of a glass bucket *e*, suspended from a platinum wire, or through a wide funnel *d*.

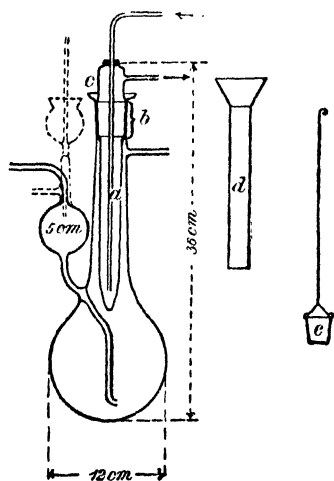



Fig. 8.

A mixture of 25 c.c. of saturated chromic acid solution, 150 c.c. of copper sulphate solution (200 g. to the litre), and 200 c.c. of concentrated sulphuric acid is the oxidising reagent employed. To carry out a determination, the liquids are filled into the flask in the order named, shaken up, cautiously heated to boiling and kept in brisk ebullition for ten minutes, the condenser being in position and supplied with running water. The flame is then removed, the purifying cylinder A connected up, and a gentle current of air sucked through for ten to twenty minutes. Next, the combustion and absorption tubes are attached and air again drawn through for five minutes. The absorption tubes are then closed, disconnected, laid in the balance case for ten minutes, momentarily opened and closed again, wiped with wash-leather or silk, laid by for another five minutes, and weighed. By this time the oxidising mixture in the flask is cool. The absorption tubes are replaced in position, the charge of metal let down into the flask, the lute at *c* made either with water or with sulphuric acid, and the liquid cautiously warmed.

From 0·5 to 5 g. of metal is weighed out, according to the content of carbon. During the oxidising process a very gentle current of air is aspirated through the apparatus. The flame should be so regulated that the contents of the flask are brought to boiling in from fifteen to twenty minutes. Brisk boiling is then kept up from one to two hours, according to the quantity and nature of the sample,

the flame then removed, and about 2 litres of air drawn through. The absorption tubes are now closed, disconnected, and weighed with the precautions described above.

Experiment has shown that when copper sulphate is present, the amount of carbon evolved as hydrocarbons is tolerably uniform for all classes of metal; it corresponds to about 2 per cent. of the total carbon. Consequently, for certain classes of routine analyses, the combustion tube can be dispensed with and the loss of carbon allowed for. It is convenient in this case to weigh out 2·77 g. instead of 2·7272 g., or 5·54 g. instead of 5·4544 g.; each 0·01 g. of carbon dioxide then indicates 0·1 per cent. or 0·05 per cent. respectively, of total carbon. When the combustion tube is absent, the U-tubes recommended by Corleis, which have obliquely placed tubulures, may be advantageously used, as the whole apparatus is then much more compact.

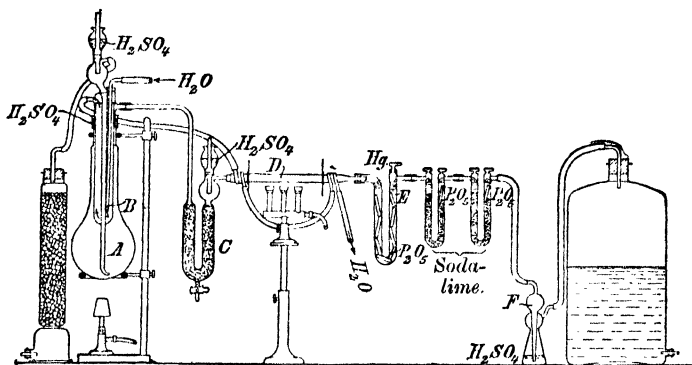



Fig. 9.

A simplified boiling flask is constructed by leading the supply tube through the condenser, which is placed outside the flask. Perhaps the best modification proposed is that of Wüst,[1] shown in Fig. 9. The supply tube runs through the condenser, but the condenser hangs inside the flask; the ground-glass junction is worked, not upon the water-jacket of the condenser, but upon an outer mantle; the height of the water-lute is thus increased to 3 to 4 cm. This arrangement has the great advantage that the flask proper can be withdrawn downwards for filling and emptying without disturbing any of the rubber connections. The drying tube C is charged with glass beads moistened with sulphuric acid, and is so designed that the acid can be replenished *in situ*. The position of the drying tube in front of the combustion tube, as here shown, is not recommended. Ledebur found that the evolved gases impart to the acid a decided odour, resembling that of

[1] *Stahl u. Eisen*, 1895, 15, 389; *J. Iron and Steel Inst.*, 1895, ii., 588.

aldehyde, from which it would appear that a part of the carbon, liberated as hydrocarbons, is retained.

Details of the method, and also of the apparatus for the conduct of this process as carried out at the works of Messrs Cammell, Laird & Co. of Sheffield, have been published by Brearly and Ibbotson.[1]

3. *Preliminary Separation of Carbon, followed by the Wet or Dry Combustion Method.* Many reagents have been suggested for dissolving out the iron and leaving the carbon behind; the separation, however, is usually incomplete, except in the methods in which copper sulphate or copper ammonium chloride is employed.

The method of separation by *Solution in Copper Sulphate* as originally worked out by Särnström, is generally recommended as accurate, as a result of the investigations of Lunge and Marchlewski, Ledebur, Wiborgh, and others. Lunge[2] employs the following six reagents for the determination :—

1. Copper sulphate, saturated solution.
2. Chromic acid, 100 g. to 100 c.c. of water.
3. Sulphuric acid, sp. gr. 1·65, saturated with chromic acid.
4. Sulphuric acid, sp. gr. 1·71, saturated with chromic acid.
5. Dilute sulphuric acid, sp. gr. 1·10.
6. Hydrogen peroxide.

The proportions of these ingredients, and the amount of metal to be weighed out, are given in the following table :—

Carbon. per cent.	Weight of Samples. g.	Copper Sulphate Solution. c c.	Chromic Acid Solution. c.c.	Sulphuric Acid. Spec. Grav.			Hydrogen Peroxide. c.c.
				1·65 c.c.	1·71 c.c.	1·10 c.c.	
Above 1·5 .	0·5	5	5	135	...	30	1
1·5 to 0·8 .	1	10	10	130	...	25	2
0·8 ,, 0 5 .	2	20	20	130	...	5	2
0·5 ,, 0·25.	3	50	45	...	75	5	2
Below 0·25 .	5	50	50	...	70	5	2

The apparatus used for the determination is the same as that described above. The metal is placed in the flask and dissolved in the cold by means of copper sulphate, with frequent agitation. The time required is at least six hours for pig iron and at least one hour for refined iron, etc.

When the reaction is ended, the condenser is inserted, the purifying, combustion, and absorption tubes connected up, and the other reagents introduced in the order :—chromic acid, strong sulphuric acid, and dilute

[1] *The Analysis of Steel Works' Materials*, p. 11.
[2] *Stahl u. Eisen*, 1891, 11, 666.

sulphuric acid. Air is then drawn through and heat gently applied. When the first effervescence has subsided, the contents of the flask are kept simmering for half an hour. The flame is then removed and hydrogen peroxide slowly dropped in ; the resulting evolution of oxygen expels all the carbon dioxide. Finally, about a litre of air is drawn through the apparatus.

Solution in Copper Potassium Chloride. Copper potassium chloride is an excellent solvent for iron, and was originally proposed by M'Creath. The method of separating carbon by this reagent, filtering off, and burning in oxygen is very generally practised. Some doubts, however, have been thrown on its accuracy, especially as regards the older methods of working.[1]

The solvent is made up by dissolving 300 g. of neutral copper potassium chloride to the litre, and may be very slightly acidulated with hydrochloric acid ; 50 c.c. is required for 1·0 g. of metal. The sample is placed in a suitable beaker, the requisite proportion of the solvent added, and the whole thoroughly agitated, first at the ordinary temperature and then after gentle warming to 40° to 50° ; or, the solution can be effected in the cold by the use of a mechanical stirring apparatus. Copper is at first precipitated, but eventually goes into solution with the formation of an inky cuproso-cupric compound ; the whole operation need not take more than an hour. The residue contains carbon, silicon, phosphorus, and sulphur, together with a little iron. It is filtered upon ignited asbestos, washed with a small quantity of the solvent, then with boiling water, and dried in the steam-bath. The potassium chloride used in making the solvent is liable to be contaminated with small amounts of organic impurities, paper fibres, etc., hence it is advisable to perform a blank determination by treating the same volume of solvent as is used for the sample in a similar manner. The combustion of the blank filter should not yield more than a milligram of carbon dioxide.

Combustion of the Residue in Oxygen. To burn the residue in oxygen, the asbestos filter containing the carbonaceous precipitate is placed in a boat and pushed into a heated combustion tube charged with copper oxide. The method used for the direct dry combustion of iron and steel as described on p. 38 should be followed. It is usual to insert in the train two additional absorption tubes, one containing ferrous sulphate solution and one containing silver nitrate to absorb traces of chlorine or hydrochloric acid in the products of combustion.

Oxidation of the Residue with Chromic Acid. As an alternative to the above method the carbonaceous residue may be oxidised by chromic acid according to Ullgren's method. The residue is filtered off into a tube 75 mm. long and 15 mm. wide, upon a pad of ignited asbestos.

[1] Cf. *Stahl u. Eisen*, 1887, 7, 13 ; 1891, 11, 50.

The filter is brought bodily into a conical flask, having a tubulure and a ground-in dropping funnel, but no condenser. The apparatus is then connected up, tested to make sure that it is air-tight, a litre of purified air drawn through, the absorption tubes attached, and the oxidising solution introduced. This consists of one volume of chromic acid solution (3 : 10) to five volumes of sulphuric acid of sp. gr. 1·83, 40 c.c. of the mixture being added for each 1·0 g. of iron. The contents of the flask are heated to boiling very slowly, over a period of one to one and a half hours, and boiled for a short time; 3 to 4 litres of purified air is then drawn through and the absorption tubes subsequently detached and weighed.

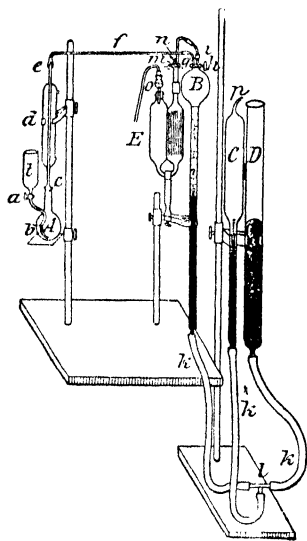



Fig. 10.

Gas-volumetric Methods for the Determination of the evolved Carbon Dioxide. The carbon dioxide produced by wet combustion may be determined gas-volumetrically instead of by absorption and weighing. Various methods and apparatus for this purpose have been described by Wiborgh,[1] Vogel,[2] Lunge and Marchlewski,[3] Reinhardt,[4] Hempel,[5] and others.

The apparatus devised by Lunge (Fig. 10) consists of a 200 c.c. flask A having a dropping funnel, also of 200 c.c. capacity, fused into the side. Into the neck is ground the inner tube of a short Liebig's condenser *d*, which, at the upper end communicates, through the ground-glass joint *e*, with the capillary tube *f* and the gas-volumeter BCD. At *a* and *c* the grinding must be so perfect that air-tight connections are secured by merely moistening with water; at *e* a ground-glass joint is not strictly necessary, and can be replaced by a rubber connection, provided care is taken that the glass surfaces are in contact. The metal is first treated with copper sulphate as above (p. 44). The apparatus is then connected up and a partial vacuum obtained by raising and lowering D six times; the stopcock *h* is then closed. The proper quantity of oxidising mixture, made up according to the table on p. 44, is then run in through *t* and *a*, the tap *a* closed, and the tap *h* opened so as to connect A and B, the levelling tube

[1] *Stahl u. Eisen*, 1887, 7, 465; *J. Soc. Chem. Ind.*, 1887, 6, 748; 1890, 9, 768.
[2] *Stahl u. Eisen*, 1891, 11, 486.
[3] *Z. angew. Chem.*, 1891, 4, 412; *J. Iron and Steel Inst.*, 1894, ii., 484.
[4] *Stahl u. Eisen*, 1892, 12, 648; *J. Iron and Steel Inst.*, 1892, ii., 511; 1893, i., 403.
[5] *Ibid.*, 1895, i., 503.

lowered, and the process of wet combustion carried out as previously described. Owing to the action of the condenser, no actual moisture gets into B, but the entering gases are saturated with aqueous vapour. After boiling, hydrogen peroxide is introduced into A (*cf.* p. 45), and the remaining air displaced by pouring in hot water until the capillary is full of liquid up to the stopcock *h*, which is then closed. The volume of air and carbon dioxide in B is measured, transferred once or twice into the Orsat pipette E, which is charged with concentrated potassium hydroxide solution, and the residual gas measured. Should the original volume of the gases be less than 140 c.c., purified air must be drawn in through *n* and *m* up to this volume, in order that readings may be obtained on the stem of the gas-burette. The use of the reduction tube C is explained fully in Vol. I., pp. 83 *et seq.*

Each cubic centimetre of carbon dioxide at 0° and 760 mm. corresponds to 0·539 mg. of carbon.

4. *Preliminary Separation of Carbon by Volatilisation of the Iron and Combustion of the Residue.* For this purpose the metal is heated either in a current of chlorine (Wöhler)[1] or of hydrochloric acid gas (Deville).

The apparatus required consists of a 1500 c.c. flask for generating the chlorine, or preferably a cylinder of compressed chlorine; a wash-bottle containing water; a second wash-bottle containing concentrated sulphuric acid; a U-tube charged with vitreous phosphoric oxide; a combustion furnace with a tube at least 16 mm. wide bent at right angles at the further end where it dips into a beaker of sulphuric acid.

The chlorine is generated from 280 g. of salt, 190 g. of pyrolusite, and 350 c.c. of dilute sulphuric acid (1 : 2). From 0·5 to 1·0 g. of metal is spread out as thinly as possible in a porcelain boat and introduced into the combustion tube. Chlorine is then passed through until the air is displaced, when the furnace is gradually heated up, finally to redness. A certain amount of chromic and manganous chlorides always remains in the boat.[2] The contents of the boat are washed into a beaker of cold water, filtered through asbestos, and oxidised either in the dry or wet way, as described above.

Neumann[3] has described a method for the combustion of the residue in a specially constructed platinum crucible.

Graphite and Temper-Carbon.—These forms of carbon are both characterised by being resistant to acids, and there is no known method of determining them separately. Temper-carbon is comparatively rare, and occurs chiefly in annealed white iron or malleable iron castings.

[1] *Chem. News*, 1867, **16**, 67.
[2] *Cf.* Hampe, *Chem. Zeit.*, 1890, **14**, 1777.
[3] *Stahl u. Eisen*, 1908, **28**, 128; *Cf.* also Mars, *ibid.*, 1909, **29**, 1155.

The method of determination described by Ledebur[1] is as follows:—

One gram of highly graphitic iron, 2 to 3 g. of light grey pig or annealed white pig iron is taken for the determination. The metal is dissolved in a suitable beaker with 25 c.c. of nitric acid of sp. gr. 1·2 for each gram of substance. During the first violent action the beaker is cooled in water. It is then digested on the sand-bath for two hours, just short of boiling, with frequent agitation. The liquid is diluted, filtered through ignited asbestos, and the black residue washed with cold water till free from iron; the filter and its contents are then either oxidised by chromic acid or dried and heated in a current of oxygen, and the carbon weighed as carbon dioxide.

Combined Carbon.—Carbide-carbon can be determined separately, whereas hardening-carbon can be obtained only by difference. The following colorimetric method of Eggertz indicates, strictly speaking, carbide-carbon only, and should be used for the determination of carbon only when the previous history (source and thermal treatment) of the samples is known and when it has been possible to secure standard samples prepared under the same conditions, in which the carbon has been determined accurately by combustion.

The method is applicable to all kinds of unhardened plain carbon steels, but not to nickel or chrome steels, because the greenish or yellowish tints of the solution interfere. It is based on the fact that when iron is dissolved in nitric acid, the combined carbon also goes into solution, with the result that the liquid is coloured more or less deeply brown. Ferric chloride, if present, affects the colour; the nitric acid used must therefore be free from chlorine. Dilution to at least 8 c.c. for each 0·1 g. of the sample eliminates the influence of the colour of the ferric nitrate. Phosphorus, sulphur, and silicon have no effect upon the accuracy of the determination. Tungsten is converted into the insoluble oxide and is filtered off, together with any graphitic carbon; the weak colours of manganese and vanadium disappear on dilution.

To carry out the determination, the solution of the metal under examination is diluted until it shows the same tint as a similarly prepared solution of a standard metal, in which the carbon has been accurately determined.

The procedure laid down by Eggertz[2] is as follows:—0·1 g. of a standard steel and the same quantity of the metal under analysis are placed in separate test tubes, 15 mm. wide and 12 cm. long, and treated with small quantities of nitric acid of sp. gr. 1·2 so long as there is any effervescence. The balance of acid is then added in the following proportions: for 0·25 per cent. of carbon, 2·5 c.c.; for 0·3 per cent., 3 c.c.; for 0·5 per cent., 3·5 c.c.; and for 0·8 per cent., 4 c.c. A slight

[1] *J. Iron and Steel Inst.*, 1891, i., 364; 1893, ii., 53; 1899, i., 368.

[2] *Chem. News*, 1881, 44, 173.

excess of acid is harmless, but a deficiency should be avoided. When the carbon content is unknown, 2·5 c.c. of acid is taken to begin with, and more is added in accordance with the colour and the amount of carbonaceous precipitate produced. The test tubes are placed through a perforated lid, in a water-bath, which is kept at the boiling point. After three-quarters of an hour all the carbon is obtained in solution and no more gas is evolved. Sometimes a red deposit, resembling a sublimate, of basic ferric nitrate forms on the sides of the vessel; this is loosened by shaking up, and filtered off if necessary; or the older method of digesting for one and a half to two hours at 80°, when the deposit is not formed may be employed. Spüller[1] hastens solution by placing the tubes in a paraffin bath heated to 135°, when five minutes suffices. Auchy[2] weighs out 1·0 g. of metal, in order to secure a fairer sample, and, after dissolving in 20 c.c. of acid, makes up to 25 c.c. and uses 5 c.c. of the solution. Whatever procedure is adopted, standard conditions must always be observed.

The test tubes, after heating, are removed from the water-bath and allowed to cool, being protected from light, which has a marked bleaching action on the colour. The contents are then transferred to colorimeter tubes of 30 c.c. capacity, graduated in twentieths of a c.c. The standard solution is so diluted with water that each c.c. corresponds to a convenient carbon percentage, say 0·02 to 0·1. Then water is added to the solution of the sample until both solutions show the same tint, care being taken to secure thorough mixing. From the volume now obtained the carbon contents of the sample under examination may be calculated. Some workers prefer to make the colorimetric comparison under exclusion of laterally impinging light. For this purpose the graduated tubes are placed in a blackened box of pyramidal shape, 26 mm. broad at the illuminated end and 12 cm. broad at the observing end, with two perforations in the upper side to receive the tubes (*cf.* Vol. I., pp. 179 *et seq.*).

Chilled steel cannot be analysed directly by Eggertz's method; by heating the sample to a temperature slightly above the critical temperature, followed by slow cooling, the hardening-carbon is converted into carbide-carbon, and the method can then be employed.

In Britton's modification[3] of Eggertz's method fifteen normal solutions, representing carbon contents of from 0·02 to 0·3 per cent., are prepared; the test solution is made up to a definite volume and compared with the nearest of the permanent standards, prepared from metallic salts. These permanent standards are now practically never used, the usual practice being to prepare a standard from a

[1] *Stahl u. Eisen*, 1899, **19**, 825; *J. Iron and Steel Inst.*, 1899, ii., 482.
[2] *J. Amer. Chem. Soc.*, 1903, **25**, 999.
[3] *Chem. News*, 1872, **26**, 139.

known carbon steel of approximately the same carbon content for use with each batch of tests.

In the colorimetric method proposed by Stead,[1] the comparison is made on the filtrates obtained after precipitating the iron as hydroxide. One gram each of the standard and of the test metal are dissolved in nitric acid of sp. gr. 1·2 at 90° to 100°; 30 c.c. of hot water and 13 c.c. of sodium hydroxide solution of sp. gr. 1·27 are added, the liquids thoroughly shaken, made up to 60 c.c., allowed to settle for ten minutes, and filtered. A 50 mm. column of the standard solution is then poured into one graduated tube and the height of the test solution in a similar tube adjusted so that the tints appear equally intense when the tubes are illuminated from below. The percentages of carbon are then inversely proportional to the lengths of the columns of liquid.

In J. H. Whiteley's[2] modification of the Eggertz test, sulphuric acid is added to the solutions, and the differences in colour of the solutions given by different steels thus reduced. The samples are dissolved in the cold in 10 c.c. of nitric acid (sp. gr. 1·2) boiled for ten minutes and cooled; 15 c.c. of sulphuric acid (1 : 3) is then added to each and the colours obtained compared as usual.

Silicon.—1. *Evaporation Method.* The quantity weighed out for analysis should be varied according to the probable content of silicon—*e.g.*, 1 g. of grey pig or cast iron; from 2 to 3 g. of white pig; and from 3 to 5 g. of malleable iron or steel. The metal is dissolved in nitric acid, evaporated to dryness, baked, taken up with hydrochloric acid, and the solution diluted and filtered. The residue is fused with fusion mixture, and the melt evaporated to dryness with excess of hydrochloric acid. On extracting with water, filtering, and igniting, the silica is obtained sufficiently pure, and is then weighed.

This two-fold evaporation is somewhat tedious, and is adopted in order that the silica may ultimately be free from iron. Though troublesome, the method gives accurate results.

When the siliceous residue obtained in the first operation is not very highly ferruginous, the further purification may be avoided as follows:—The impure silica is ignited and weighed; it is then evaporated with hydrofluoric acid and a few drops of sulphuric acid, ignited, and weighed again; the difference between the two weighings represents the silica. If the residue is considerable, it is advisable to treat it with ammonium carbonate so as to make sure that all sulphuric acid is completely volatilised.

2. *Blum's Method.*[3] The metal is dissolved in hydrochloric acid containing bromine, and evaporated to dryness, after addition of twice

[1] *J. Iron and Steel Inst.*, 1883, i., 213; *Chem. News*, 1883, **47**, 285.
[2] *Iron and Steel Inst., Carnegie Schol. Memoirs*, 1917, **8**, 81.
[3] *Stahl u. Eisen*, 1885, **5**, 594; *Chem. News*, 1886, **53**, 300.

its weight of ammonium chloride, whereby the drying is facilitated. The residue, after lixiviation, is washed on the filter alternately with cold water and with hot 50 per cent. hydrochloric acid. The silica thus obtained is of a pure white colour, and leaves no residue on treatment with hydrofluoric acid.

3. *Drown's Method.*[1] The metal is dissolved in nitric acid of sp. gr. 1·2. When all action has ceased, about 25 to 30 c.c. of dilute sulphuric acid (1 : 3), or 35 to 40 c.c. of 1 : 4 acid (Ledebur), is added and evaporated on a sand-bath or hot-plate until all the nitric acid is expelled and copious white fumes of sulphur trioxide are evolved. The cooled residue is lixiviated with 100 c.c. of water, warmed till the ferric sulphate has gone into solution, and filtered. The mixture of carbon and silica on the filter is thoroughly washed with cold water, then with four successive portions of hot hydrochloric acid (sp. gr. 1·12), and finally with hot water. After ignition the silica should be pure white in colour; ignition for two to three hours at a full red heat may be necessary with cast iron, etc., if much graphite is present.

A modification suggested by Strick[2] consists in evaporating down the metal with dilute sulphuric acid alone, in a beaker; when a cold clock-glass laid on the beaker shows that no more water vapour is being evolved, the residue is cooled, lixiviated, and treated as above.

Ferro-silicon is sometimes resistant both to nitric acid and to hydrochloric acid containing bromine. It is then necessary to mix 0·2 to 0·3 g. with fifteen times its weight of sodium carbonate and sodium peroxide mixture (1 : 2) in a nickel crucible and very gradually heat to fusion, when the alloy is readily decomposed. The melt is then extracted and evaporated with hydrochloric acid. With high silicon alloys great care is necessary to avoid loss during the fusion, as the reaction with sodium peroxide is very violent. If the sample is thoroughly ground to the finest possible state of subdivision it may be completely decomposed by first warming with strong aqueous caustic soda in a nickel or silver basin, then evaporating slowly to dryness, and finally fusing the residue with the addition of only a small quantity of sodium peroxide.

Brearley and Ibbotson[3] give the following method for the determination of silicon in ferro-silicon, which gives excellent results. Two grams of the finely ground sample is dissolved in 50 c.c. of concentrated hydrochloric acid, to which is added 10 to 20 c.c. of nitric acid, the solution boiled for not less than fifteen minutes, made up with water to 200 c.c. and filtered without delay. The residue is washed with cold dilute hydrochloric acid, ignited strongly for at least thirty minutes,

[1] *Chem. News*, 1880, **42**, 299; 1884, **60**, 20.

[2] *Dingl. polyt. J.*, **252**, 384; *J. Iron and Steel Inst.*, 1887, i., 465.

[3] *The Analysis of Steel Works' Material*, p. 117.

and then allowed to cool in the desiccator and weighed quickly. If this method is accurately followed, an addition of 0·1 per cent. as a correction for the soluble silica will give results more nearly approximating the actual silicon content than more elaborate methods.

It is to be noted that all these methods make no distinction between silicon combined with iron and silica present in the form of enclosed slag. The point is of little technical importance, but in scientific investigations the determination of silicon proper may be required. This is done, according to Turner,[1] by igniting in a current of chlorine, collecting the vaporised ferric chloride and silicon tetrachloride in water, evaporating the solution, taking up with acid, filtering off the silica, and igniting and weighing as usual. Any enclosed slag or cinder is thus left behind in the boat, and may be collected, examined, and weighed.

Manganese.—All the methods described for determining manganese in iron ores are applicable to iron and steel (*cf.* pp. 7 and 29); several of them were originally worked out for iron and subsequently modified for the analysis of ores. Several methods, however, chiefly volumetric, are better adapted for the determination of manganese in metal than in ores.

Cast iron and ordinary steels usually contain less than 1·0 per cent. of manganese; spiegel about 20 per cent., and ferro-manganese about 80 per cent. As a rule, 1 g. is a sufficient quantity to weigh out for analysis; in the case of highly manganiferous irons, 0·5 g., or even less, is enough. Malleable iron is generally so low in manganese that from 2 to 3 g. may be required.

Hydrochloric acid is used for dissolving the metal; if there is a considerable residue, as in the treatment of grey pig, it may be rendered soluble by fusion with alkali. Whenever manganese is determined gravimetrically, the silica must be rendered insoluble by evaporation to dryness, and may be filtered off or not, as occasion demands.

The following are among the more important volumetric methods:—

1. *The Volhard-Wolff Permanganate Method* (*cf.* p. 29). The sample is weighed into a covered porcelain dish or into a conical flask about 75 mm. wide at the base, dissolved in 15 c.c. of nitric acid of sp. gr. 1·2, and evaporated to dryness. The mass is taken up with 20 c.c. of hydrochloric acid, boiled with 3 g. of potassium chlorate until free from chlorine, diluted, filtered into a litre conical flask, and the residue washed with water containing hydrochloric acid. The liquid is then treated with zinc oxide and the determination completed as described on p. 30.

[1] *Chem. News*, 1884, 49, 233.

When there are many determinations to be carried out, time is saved by using the modified method proposed by v. Reis.[1] One gram of iron is dissolved in 25 c.c. of a mixture consisting of 275 volumes of water, 125 of nitric acid (sp. gr. 1·4) and 100 of concentrated sulphuric acid. The solution is boiled over a free flame until fumes of sulphuric acid appear, allowed to cool, diluted with 100 c.c. of water and 10 c.c. of the acid mixture, warmed to dissolve the salts, and transferred to a litre conical flask. The carbon is then oxidised by adding 3 g. of barium peroxide and 5 c.c. of concentrated nitric acid, and the excess of peroxide destroyed by boiling. The liquid is diluted with 300 to 400 c.c. of hot water, treated with zinc oxide, and titrated with permanganate; v. Reis prefers to add excess of permanganate and titrate back with a solution of manganous sulphate equivalent to the standard permanganate.

2. *The Hampe and Ukena Chlorate Method.*[2] This method takes advantage of the fact that manganese peroxide is precipitated from manganese salts on boiling with nitric acid and potassium chlorate. The precipitate is never free from iron, and cannot, therefore, be weighed for a gravimetric determination. Iron does not interfere in the volumetric method, but cobalt, lead, and bismuth, if present, are partially precipitated and affect the results; the precipitate is then dissolved by means of nitric and oxalic acids and reprecipitated with chlorate. Copper, nickel, tin, and phosphorus have no injurious effect. The main requirements are:—1, That the solution be very concentrated; 2, that sulphuric acid, if present in more than moderate quantity, be removed by adding barium nitrate; and 3, that hydrochloric acid be absent.

For the determination, the metal is dissolved in 70 c.c. of nitric acid of sp. gr. 1·2, in a 500 c.c. flask, the hot, clear solution allowed to cool, 11 g. of potassium chlorate crystals added through a wide-neck funnel, and the liquid gently boiled for from twenty-five to forty minutes down to a volume of 30 to 40 c.c. In the analysis of ferro-manganese the concentration must be carried to the furthest possible limit. By this time all chlorine should have been boiled away; this is essential for the success of the precipitation. If the liquid is boiled too violently, the precipitate is apt to become slimy and difficultly soluble.

Grey pig iron is treated with 50 c.c. of acid in a beaker and evaporated to half the volume. The liquid is cautiously diluted with hot water without disturbing the sediment, filtered into a flask, evaporated, and treated with chlorate as above.

The concentrated liquid is next very carefully diluted with water and cooled. The supernatant liquid is first filtered through a close

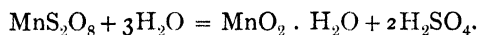
[1] *Z. angew. Chem.*, 1892, **5**, 604, 672; *J. Soc. Chem. Ind.*, 1893, **12**, 378.
[2] *Chem. Zeit.*, 1885, **9**, 1083; *J. Iron and Steel Inst.*, 1885, ii., 652.

asbestos filter, and, when all the liquid has passed through, the precipitate is collected; washing is continued until the filtrate no longer reacts with starch and potassium iodide. The filtrate is tested for manganese by boiling with chlorate, when there should be no further precipitation; or, preferably, a portion is boiled with nitric acid and lead or bismuth peroxide and filtered through asbestos, when the presence of manganese is indicated by the formation of permanganic acid.

Ten c.c. of standard ferrous ammonium sulphate solution is then run into the flask from a burette, whereby any adherent manganese peroxide is dissolved. The filter is transferred to the flask with a little water and disintegrated by shaking and stirring. A further quantity of standard solution is run into the flask, so that all the manganese is dissolved, the total volume read off, dilute sulphuric acid (1 : 3) added to the solution, and the excess of ferrous ammonium sulphate titrated back with standard permanganate.

The permanganate solution must be standardised under the conditions of the assay. For this purpose 0·1 g. of chemically pure potassium permanganate is dissolved in 60 c.c. of nitric acid of sp. gr. 1·2 with the aid of a few crystals of oxalic acid, and precipitated as above. The strength of the standards should be such that 1 c.c. corresponds to from 1 to 5 mg. of manganese. Oxalic acid may be used as the reducing solution in place of ferrous ammonium sulphate.

3. *G. v. Knorre's Persulphate Method.*[1] On boiling manganese sulphate in acid solution with ammonium persulphate, the manganese is precipitated as hydrated peroxide, since manganese persulphate is stable only in the cold. The reaction is as follows:—

$$MnS_2O_8 + 3H_2O = MnO_2 . H_2O + 2H_2SO_4.$$

The precipitate is too impure to be weighed, and must be determined volumetrically by means of standard ferrous ammonium sulphate and potassium permanganate solutions. These solutions should be standardised from mixtures of manganese and iron salts containing these metals in approximately the same proportions as in the test.

To carry out the determination, the metal is dissolved in a beaker in 50 to 60 c.c. of warm dilute sulphuric acid (1 : 10) and filtered into a 500 c.c. conical flask. Highly siliceous ferro-manganese leaves a manganiferous residue, which is evaporated in a platinum crucible with sulphuric and hydrofluoric acids, dissolved in a little water, and added to the original solution. Ammonium persulphate solution (60 g. per litre) is then added to the liquid, in the proportion of 150 c.c. or 250 c.c., according as less or more than 1 g. of metal was weighed out, and the volume diluted to from 250 to 300 c.c. After boiling for fifteen

[1] *Z. angew. Chem.*, 1901, 14, 1149; 1903, 16, 905.

minutes, the liquid is allowed to settle, and filtered, with the usual precautions, upon a dense filter of 8 cm. diameter, or on a double filter. The precipitate is then treated as described under method No. 2.

Lüdert[1] dissolves from 2 to 4 g. of the sample in from 25 to 50 c.c. of nitric acid of sp. gr. 1·2. The solution is heated to boiling and diluted with 400 c.c. of water without filtering; 40 c.c. of sulphuric acid and 50 c.c. of ammonium persulphate are then added. After boiling for half an hour to decompose the manganese persulphate and the excess of ammonium persulphate, the solution is cooled by placing the flask in cold water, and 5 c.c. of a standardised solution of hydrogen peroxide added. When the whole of the manganese peroxide has gone into solution, the excess of hydrogen peroxide is titrated back with permanganate. It is necessary to standardise the hydrogen peroxide solution with the permanganate each day on account of its instability.

In presence of tungsten the method is modified as follows[2]:—From 2 to 10 g. of tungsten steel is dissolved in dilute sulphuric acid in absence of air, the solution gradually heated to boiling, and boiled for a few minutes. After cooling, the residue containing the tungsten is filtered off as rapidly as possible, as it oxidises fairly readily in the air and would then go into solution, washed two or three times with water, and the manganese determined in the filtrate as described. The precipitate of hydrated manganese peroxide must be dissolved by ferrous sulphate, not by hydrogen peroxide; the latter acts upon any traces of tungsten that may be present in the solution, and thus leads to high results for the manganese.

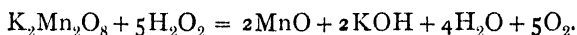
4. *Persulphate Oxidation Method.* A method much in vogue in steel works' laboratories in which a large number of manganese determinations in plain carbon steels has to be made daily, consists in dissolving 0·2 g. of the sample in 10 c.c. of nitric acid of sp. gr. 1·2 in a boiling-tube. Several of the tubes are then placed in boiling water until solution is complete and all nitrous oxide fumes expelled. Fifteen c.c. of silver nitrate solution (1·33 g. per litre) is then added to the contents of each tube, together with 1 g. of slightly moist ammonium persulphate crystals. The tubes are replaced in the water-bath, which is kept boiling until the manganese is oxidised to permanganate and the action of the persulphate is no longer apparent. A small additional quantity of persulphate is added to the contents of each tube, and the tubes are then cooled in water. The permanganate formed is determined colorimetrically (p. 57) or by titration with sodium arsenite solution, which is run in from a graduated burette, the solution being titrated in a porcelain dish; the reaction is completed when the colour

[1] *Z. angew. Chem.*, 1904, 17, 422.
[2] G. v. Knorre, *Stahl u. Eisen*, 1907, 27, 380.

of the permanganate is discharged and a pale greenish coloration formed. The arsenite solution is made up from a stock solution containing 5 g. of arsenious acid and 15 g. of sodium bicarbonate per litre; 80 c.c. of this solution is diluted to 1000 c.c. for the titration. The value of the arsenite solution is obtained by titrating a solution of 0·2 g. of steel of known manganese content (Lambert).[1]

5. *Bismuthate Method.* This method of determining manganese is now largely used in technical laboratories for all classes of pig iron and cast iron, and also for steels containing more than 0·8 per cent. of manganese, and not more than 1·5 per cent. chromium. One gram of steel, or 0·5 g. if the amount of manganese present is over 1 per cent., is dissolved in nitric acid of sp. gr. 1·2. The nitrous fumes are boiled off and small quantities of sodium bismuthate are added until a permanent permanganate colour results which persists on boiling for a few minutes; this renders certain the oxidation of the carbon. A few drops of sulphurous acid solution are now added and the solution is boiled until clear and free from fumes. The solution is diluted to not more than twice its original volume, cooled to room temperature, and then half a gram of sodium bismuthate is added and the solution well shaken. The excess of bismuthate is filtered off through asbestos which has been previously ignited and is washed with 5 per cent. nitric acid. To the permanganate solution thus obtained a known volume of standard ferrous ammonium sulphate is added until the pink colour has disappeared and the excess of ferrous iron is titrated with standard permanganate. The solution may also be titrated with a standard solution of sodium arsenite as described in method No. 4. When more than a trace of chromium is present filtration should not be delayed after addition of the sodium bismuthate.

6. *Oxidation by Peroxides.* Schneider[2] oxidises the manganese to permanganic acid and titrates back with hydrogen peroxide. The decomposition takes place in accordance with the equation:—

$$K_2Mn_2O_8 + 5H_2O_2 = 2MnO + 2KOH + 4H_2O + 5O_2.$$

Two grams of steel or pig iron is dissolved in 200 c.c. of nitric acid of sp. gr. 1·2 and heated to boiling with a considerable excess of lead peroxide or bismuth oxide. The liquid is immediately cooled down, filtered through asbestos, and titrated with hydrogen peroxide diluted with two or three volumes of water, the strength of which has been determined by means of standard permanganate. Lead peroxide is apt to be manganiferous, and must be tested by decomposing a sample with hot sulphuric acid, cooling, diluting, and warming with a fresh

[1] *Cf.* also P. Smith, *Chem. News*, 1904, **90**, 237; Rubricius, *Stahl u. Eisen*, 1905, **25**, 890; 1910, **30**, 957.

[2] *Dingl. polyt. J.*, 1888, **269**, 224; *J. Iron and Steel Inst.*, 1892, ii., 512.

portion of the peroxide; manganese, if present, will then produce a more or less pink solution. Steels containing chromium cannot be examined by this method.

7. *Colorimetric Method.* When a permanganic solution has been prepared as described under method No. 4, the manganese can be determined by comparing the tint with a solution obtained from a standard steel of known manganese content. To carry out the determination, 0·2 g. of metal is dissolved in 10 c.c. of nitric acid of sp. gr. 1·2 in a boiling tube placed in a water-bath, and boiled to expel nitrous fumes. Silver nitrate and ammonium persulphate are added as described on p. 55. After cooling, the standard solution is diluted to a definite volume somewhat lighter in tint than the test solutions, which are compared with it, diluted to match, and measured in the usual way.

Sulphur.—The methods for the determination of sulphur fall into three classes:—

1. Evolution of the sulphur as sulphuretted hydrogen and determination *via* metallic sulphides.
2. Evolution of the sulphur as sulphuretted hydrogen and conversion into barium sulphate.
3. Direct precipitation as barium sulphate.

1. *Evolution of the Sulphur as Sulphuretted Hydrogen and Determination* via *Metallic Sulphides.* In these methods the sulphuretted hydrogen is absorbed without oxidation; the sulphides thus formed are determined either gravimetrically, volumetrically, or colorimetrically. The last method gives only approximate results, but the two former are very accurate.

Gravimetric Method. Silver, lead, copper, and cadmium salts have been proposed for the gravimetric absorption of sulphuretted hydrogen Silver and copper salts, however, have been shown by Schulte[1] to be unsuitable, since gases other than sulphuretted hydrogen are evolved. which yield metallic silver with silver acetate and a yellow precipitate, containing phosphorus with copper acetate. Schulte found cadmium acetate, first proposed by Wiborgh, to be the best absorbent. The precipitated sulphide may be weighed as such on a tared filter or converted into copper sulphide and ultimately weighed as cupric oxide. The absorbent is made by dissolving 25 g. of cadmium acetate in a mixture of 250 c.c. of acetic acid and 250 c.c. of water on the water-bath, diluting to a litre, and filtering; or an ammoniacal solution containing 25 g. of cadmium acetate, and 100 c.c. ammonium hydroxide per litre may be used. The solution for converting the cadmium sulphide into copper sulphide is made by dissolving 120 g. of crystallised copper sulphate in 800 c.c. of water and 120 c.c. of concentrated sulphuric acid and diluting to one litre.

[1] *Stahl u. Eisen*, 1896, **16**, 867; *Chem. News*, 1897, **75**, 47.

The apparatus for carrying out the determination is very simple, consisting of a flask fitted with a thistle funnel and delivery tube leading into a U-tube or beaker containing the cadmium solution. The use of the carbon dioxide generator and combustion furnace formerly employed is superfluous.

To carry out the determination, 5 to 10 g. of the sample is placed in a 500 c.c. round bottomed flask, and 30 to 35 c.c. of the cadmium acetate solution in the receiver. Fifty c.c. of hydrochloric acid (2 : 1) is then run in from a thistle funnel, 25 c.c. being first added, and the remaining 25 c.c. after a short interval if the action is not too violent; a further 50 c.c. is subsequently added, similarly, making a total of 100 c.c. of acid. The decomposition is regulated so that three to four bubbles of gas are evolved per second; this is readily effected by employing a luminous flame provided with a regulator for the heating. When the solution of the steel is complete, the flame is raised gradually until the solution approaches the boiling point, and the solution heated to boiling for a minute. The contents of the absorption vessel are then filtered and the cadmium sulphide washed and weighed or treated with 5 c.c. of the copper solution, prepared as described above, the precipitate collected on an ash-free filter paper, washed with slightly acidulated water, and ignited to cupric oxide in a platinum dish. The weight of $CuO \times 0{\cdot}403 = S$.

Volumetric Method. In the volumetric method, as worked out by Reinhardt,[1] the cadmium sulphide is filtered off, treated with standard iodine and hydrochloric acid, and the excess of iodine titrated back with sodium thiosulphate.

The precipitate of cadmium sulphide is filtered, washed with ammonia (1 : 3), the filter paper and precipitate returned to the original flask, 30 to 50 c.c. of standard iodine solution added, then 20 c.c. of hydrochloric acid (1 : 1) and 200 c.c. of water, and the solution titrated back with sodium thiosulphate, after the addition of starch solution. 1 c.c. $N/10$ iodine $= 0{\cdot}001603$ g. sulphur.

The liquid containing the cadmium sulphide in suspension may be acidified with hydrochloric acid in the cold and titrated with standard iodine after the addition of starch. In a variant of this method the hydrogen sulphide is absorbed in dilute sodium hydroxide solution and titrated with iodine, after acidifying the solution with hydrochloric acid, using starch as an indicator.

2. *Evolution of the Sulphur as Sulphuretted Hydrogen, and Conversion into Barium Sulphate.* The apparatus employed in this method is shown in Fig. 11. Ten grams of the sample is introduced into the decomposition flask, the contained air displaced by carbon dioxide,

[1] *Stahl u. Eisen*, 1906, **26**, 800.

and then 50 c.c. of hydrochloric acid, saturated with bromine, placed in the absorption bulb.

The metal is dissolved by the addition of 100 c.c. of hydrochloric acid of sp. gr. 1·19, the solution boiled for five minutes, and a current of carbon dioxide passed through for a further ten minutes. The contents of the absorption bulb are then washed out into a porcelain dish, 5 c.c. of sodium carbonate solution (1 : 10) added, the whole evaporated to dryness, taken up with 10 c.c. of hydrochloric acid (1 : 1) and water, and filtered. The solution is precipitated as usual with barium chloride, and the resulting barium sulphate ignited and weighed; any content of sulphur in the bromine and hydrochloric acid must, of course,

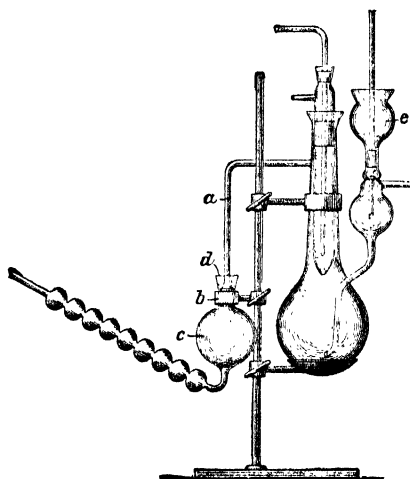
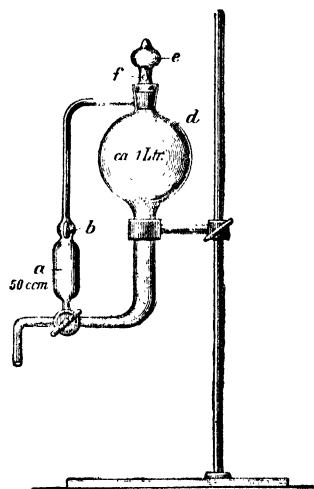



FIG. 11. FIG. 12.

be determined by a blank experiment and deducted. The weight of $BaSO_4 \times 13{\cdot}744$ gives the percentage of S.

The apparatus shown in Fig. 12 was devised by Corleis for measuring off the mixture of bromine and hydrochloric acid.

3. *Direct Precipitation as Barium Sulphate.* Krug,[1] Meinecke,[2] and Phillips[3] have pointed out independently that there are two sources of error in all methods of determining sulphur in iron and steel which depend on its liberation as sulphuretted hydrogen. On the one hand the whole of the sulphur is not evolved as sulphuretted hydrogen dimethyl sulphide, $(CH_3)_2S$, being also formed, and on the other hand a portion remains behind, partly as iron (and copper) sulphide. The method of "annealing" has been proposed by Macfarlane and Gregory[4]

[1] *Stahl u. Eisen*, 1905, **26**, 887.
[2] *Z. angew. Chem.*, 1888, **1**, 377.
[3] *J. Soc. Chem. Ind.*, 1896, **15**, 218.
[4] *Chem. News*, 1906, **93**, 201.

to overcome the first difficulty. Five grams of drillings are mixed with 0·5 g. of cream of tartar, wrapped in a filter paper and heated to a bright red heat for fifteen minutes in a covered porcelain crucible. When cold the mass is powdered, placed in the evolution flask and treated as usual. To avoid these sources of error entirely, however, the only method is to oxidise the sulphur completely to sulphuric acid during solution and to precipitate it as barium sulphate. The results obtained by this method are inaccurate unless certain precautions are adopted, while the method is somewhat lengthy to be used where numerous determinations are required.

The following form of this method has been worked out by Krug.[1] Five grams of the sample is dissolved in 50 c.c. of nitric acid of sp. gr. 1·4 in a 500 c.c. round-bottom flask. The solution is first warmed gently until the evolution of nitrous fumes has ceased, and then gradually heated to boiling; solution is complete in one to two hours. To prevent any volatilisation of sulphuric acid when the ferric nitrate is subsequently baked, 0·25 g. of pure potassium nitrate is added, which retains the free sulphuric acid as potassium sulphate. The solution is evaporated to dryness, baked, the residue dissolved in hydrochloric acid, evaporated till chlorine ceases to be evolved, the silica and insoluble matter filtered off, the filtrate concentrated, and the bulk of the iron removed by the ether extraction method (p. 6). The sulphuric acid is then precipitated with barium chloride in the residual solution.

In dealing with tungsten steels, care must be taken that no tungstic acid passes into the filtrate containing the sulphur. This may occur if too much hydrochloric acid is left when the insoluble matter is filtered off.

Two opposing defects are inherent in this method. The barium sulphate is precipitated incompletely in presence of a large excess of acid, and precipitates from only moderately acid solutions tend to carry down more or less iron with them. These errors may be made to compensate each other to a considerable extent (*cf.* Vol. I., p. 368).

The above method is frequently modified by dissolving 5 g. of the sample in a mixture of 20 c.c. hydrochloric acid and 30 c.c. nitric acid in a tall beaker, evaporating to dryness and baking, taking up with 40 c.c. hydrochloric acid and again evaporating until a skin appears, which is redissolved in dilute hydrochloric acid. The solution is diluted to 50 c.c., filtered hot, and the residue washed. The filtrate is then boiled, 20 c.c. of hot 10 per cent. barium chloride solution added a little at a time, and boiling continued for a few minutes. The solution is allowed to stand for several hours and the barium sulphate filtered off, washed and weighed as usual. A blank experiment should be made.

[1] *Stahl u. Eisen*, 1905, **26**, 887.

According to Platz,[1] 5 g. of pig iron is dissolved in nitric acid of sp. gr. 1·2, evaporated to dryness with hydrochloric acid, the residue dissolved in hydrochloric acid, the solution evaporated to syrupy consistency, diluted, filtered, and precipitated cold with barium chloride. After standing at the ordinary temperature for twelve hours, the barium sulphate is filtered off, washed with cold water, and burnt wet. Were the solution precipitated boiling, the barium chloride solution, which is apt to become basic during the evaporation, would precipitate a considerable quantity of the iron. In any case, a little iron, owing to adsorption by the filter, will be found in the ignited precipitate. The latter is, therefore, treated with a little hydrochloric acid and boiled with water and a drop of barium chloride, when pure white barium sulphate, free from iron, is obtained.

Tamm[2] dissolves 5 g. of metal by boiling with 50 c.c. of water and 10 g. of potassium chlorate, after first adding 1 c.c. of hydrochloric acid to start the reaction; 5 c.c. of hydrochloric acid is then added, and further successive portions, each of 5 c.c., until there is no further evolution of chlorine and the metal is completely dissolved. The precipitation is then effected with barium chloride in the warm solution and the precipitate treated as above.

Phosphorus.—Phosphorus is determined in iron and steel in the same manner as in iron ores (p. 16). Two points have to be specially taken into consideration; the silicon must be entirely eliminated as silica, and the phosphorus must be fully oxidised to phosphoric acid. Any arsenic present should be eliminated by treatment of the hydrochloric acid solution with metallic zinc. Complete removal of arsenic is assured by the addition of ammonium bromide after treatment with zinc and evaporating to dryness.

The amount of metal to be weighed out depends on its nature; of pig iron for the basic process 0·5 g. is taken; of cast and puddling iron 1 to 2 g.; and of iron for the acid process and steels 2 to 5 g.

1. *The Ignition Method.* The metal is dissolved, in a porcelain dish covered with a clock-glass, in 25 to 80 c.c. of nitric acid of sp. gr. 1·2, the solution evaporated to dryness, and the nitrates decomposed by heating the residue on a wire gauze over the free flame. The silica is thus rendered insoluble, and the phosphorus is converted into phosphoric acid. The mass is warmed with 10 to 20 c.c. of concentrated hydrochloric acid, zinc added to eliminate any arsenic present, and the liquid evaporated to syrupy consistency; 10 c.c. of nitric acid and (after a few minutes) hot water are added, the solution filtered, and the residue washed with dilute nitric acid. The filtrate, which should amount to about 100 c.c., is neutralised with ammonia, 1 g. of ammonium

[1] *Stahl u. Eisen*, 1887, 7, 256; *J. Iron and Steel Inst.*, 1887, i., 471.
[2] *J. Iron and Steel Inst.*, 1887, ii., 369.

nitrate added, then heated nearly to boiling and precipitated with 25 c.c. of molybdate reagent; fifteen minutes at 80° to 90° are allowed for complete precipitation. The phospho-molybdate is then filtered off, washed with nitric acid (1 : 1), dissolved in dilute ammonia (*cf.* p. 18), and precipitated hot with 2 c.c. of magnesia mixture, the further procedure being the same as in the analysis of ores. Should the solution be tinged green owing to the presence of reduced molybdic acid, this is oxidised by adding a few drops of hydrogen peroxide.

2. *The Oxidation Method* (v. Reis [1]). The metal is dissolved in nitric acid and 25 c.c. of permanganate solution (10 g. to the litre) added, together with 8 to 10 g. of ammonium chloride, which effects the re-solution of precipitated manganese peroxide. The liquid is boiled until clear, evaporated to dryness, and proceeded with as in the ignition method.

The following rapid method is used in many iron works' laboratories.[2] Five grams of steel is dissolved, oxidised with permanganate, evaporated to 25 c.c., and rinsed into a 400 c.c. conical flask. Ammonia is added very gradually, with continual agitation, in slight excess, and the solution then acidified with nitric acid until the liquid is clear, and the temperature brought up to about 90°. After adding 40 c.c. of molybdate solution, the flask is closed with a rubber stopper, wrapped in a thick cloth, and thoroughly shaken. The precipitate is allowed to settle, filtered off, and determined either by direct weighing or by titration, as described on pp. 18 and 32.

In pig irons containing titanium the residue insoluble in nitric acid includes the titanium, together with some of the phosphorus. The latter may be recovered by igniting the residue, fusing with sodium carbonate, and extracting with water. Sodium phosphate is dissolved and sodium titanate remains insoluble.

Tungsten steels require a mixture of nitric and hydrochloric acids for solution, and the tungstic acid residue should be treated to remove phosphorus. The tungstic acid is dissolved in ammonia, a little ferric chloride added to the solution, which is made slightly acid with hydrochloric acid. The iron is precipitated with ammonia and carries down the phosphorus. This precipitate is filtered, redissolved and reprecipitated, then dissolved in hydrochloric acid, and the solution added to the main bulk of ferric chloride solution for subsequent treatment.[3]

The molybdate precipitate obtained from vanadium steels by the usual methods is orange red, and contains some vanadium and not all the phosphorus. Accurate results are obtained by the following

[1] *J. Iron and Steel Inst.*, 1887, ii., 365.
[2] *Cf.* Blair, *The Chemical Analysis of Iron*, p. 88.
[3] T. E. Rooney and L. M. Clark, *J. Iron and Steel Inst.*, 1926, i., 457; *J. Soc. Chem. Ind.*, 1926, 45, 493.

method, due to Johnson.[1] 1·63 g. is dissolved in 45 c.c. of nitric acid (sp. gr. 1·13). The solution is boiled, 3 c.c. of 5 per cent. permanganate solution added, and then after boiling, a slight excess of ferrous sulphate. A further 50 c.c. nitric acid of sp. gr. 1·42 is added, the liquid boiled, and then stirred with 50 c.c. of a solution containing 55 g. ammonium molybdate, 50 g. ammonium nitrate, and 40 c.c. ammonia sp. gr. 0·95 per litre, and allowed to settle overnight.

Copper.—The majority of the methods for determining copper in iron and steel depend upon the separation of the copper as sulphide. When the sample is dissolved to a ferrous salt in dilute sulphuric or hydrochloric acid, all or some of the copper remains undissolved. If, on the other hand, oxidation occurs during the solution, there is so much ferric salt formed, that direct treatment with sulphuretted hydrogen is out of the question. A previous reduction of the iron is therefore necessary before precipitating the copper.

1. *Gravimetric Method.* At least 10 g. of metal is dissolved in 100 c.c. of hydrochloric acid of sp. gr. 1·19, with the aid of nitric acid, potassium chlorate, or hydrogen peroxide, and the solution evaporated to 50 c.c. The solution is reduced by means of 5 g. of sodium hypophosphite at boiling temperature; this salt does not react with sulphuretted hydrogen, so that an excess is of no consequence. Sulphuretted hydrogen is passed into the warm solution[2] until saturated, and the precipitate, together with the original residue, filtered off and washed with hot water. It is then washed into a beaker, the filter ash added, the whole boiled with hydrochloric acid of sp. gr. 1·19 and 1 to 2 g. of potassium chlorate till completely dissolved, and the solution evaporated to dryness; the silica is filtered off, the copper precipitated as sulphide in the filtrate and weighed, after ignition; or else the filtrate is freed from chlorides by evaporating with sulphuric acid and then electrolysed.

A simpler method is to dissolve the steel in dilute sulphuric acid, and boil, without filtering, with about 10 g. sodium thiosulphate. This effects the reduction of any ferric salt and precipitates dissolved copper as sulphide together with free sulphur.

The precipitate is filtered and ignited and the determination finished either electrolytically or colorimetrically as described below.

2. *Electrolytic Method.* Ten to twenty grams of drillings are treated with 40 c.c. of dilute sulphuric acid, and a further 40 c.c. is added after the first reaction is completed.[3] When solution is complete, the liquid is diluted to 200 c.c. and filtered. The residue is ignited in a porcelain crucible, dissolved in fuming nitric acid, evaporated with

[1] *Ind. Eng. Chem.*, 1919, **11**, 113; also *Chem. News*, 1919, **118**, 113.
[2] *Cf.* Reinhart, *Stahl u. Eisen*, 1889, **9**, 404.
[3] *Cf.* Zinberg, *Z. anal. Chem.*, 1912, **51**, 19.

sulphuric acid until fumes are evolved, taken up with 20 c.c. of nitric acid of sp. gr. 1·2 and 20 c.c. of water, filtered, diluted to 120 c.c., and electrolysed with a current of 0·5 to 1·0 ampère per sq. dcm.

3. *Colorimetric Method.* This method, as described by Ziegler, has been modified by Perillon.[1] Solutions obtained by adding an excess of ammonia to copper nitrate are compared for depth of tint. The standard is made up by dissolving electrolytic copper in nitric acid and adding just enough ammonia to redissolve the precipitate. It is desirable to have two standards at hand, containing 2·0 and 0·2 mg. of copper per cubic centimetre, respectively.

The test solutions are prepared by precipitating the copper as sulphide and dissolving it in nitric acid. Colorimeter tubes, as employed for Eggertz's carbon assay, are used, and the test is diluted until it attains the tint of the standard (*cf.* p. 49). The method is very delicate, and is especially adapted to the estimation of very small amounts of copper.

Potassium ferrocyanide gives a very sensitive test with copper solutions, and it is possible by this means to detect 1 part of copper in 2 million parts of water. Iron must be absent and the solutions must be neutral; they are suitably prepared by boiling off the excess of ammonia from ammoniacal copper solutions.

Arsenic.—Arsenic may be determined either by precipitation as arsenic sulphide and converting this into magnesium pyroarsenate, or by distillation as arsenic trichloride and subsequent precipitation with magnesia mixture or titration of the distillate with iodine. When iron is dissolved in hydrochloric acid, arsine is not evolved, unless the solution is made very acid. According to v. Ries,[2] arsenic may be relied upon not to escape as arsine when dilute sulphuric acid (1 : 5) is used.

1. *Sulphide Method.* Ten to fifty grams of metal is dissolved in hydrochloric acid of sp. gr. 1·19 and precipitated by means of sulphuretted hydrogen, as for the determination of copper. The sulphides are dissolved, the silica and graphite filtered off, and the filtrate warmed with a slight excess of potassium hydroxide and sodium sulphide; the copper is thus precipitated, whilst arsenic remains in solution. The filtrate is acidified with hydrochloric acid and violently agitated for a few minutes. The precipitated arsenic sulphide is filtered, washed, and oxidised with hydrochloric acid and potassium chlorate. The solution is again filtered through a small filter paper, the filtrate concentrated to a few cubic centimetres, tartaric acid and an excess of ammonia added (which should produce no precipitate), and the arsenic precipitated with magnesia mixture. At least twenty-four

[1] *Dingl. polyt. J.*, 1892, **285**, 142.
[2] *Stahl u. Eisen*, 1889, **9**, 720.

hours at the ordinary temperature is required to complete the precipitation of ammonium magnesium arsenate. The precipitate is treated exactly like the corresponding phosphorus compound, and is finally weighed as $Mg_2As_2O_7$. v. Reis[1] states that if the quantity of arsenic present is not too small, vigorous stirring and subsequent standing for fifteen minutes suffices to ensure the complete precipitation of the arsenic.

2. *Distillation Method.* From 5 to 50 g. of steel is treated with 50 per cent. hydrochloric acid in a flask, the gas evolved being passed into bromine water to collect any arsenic evolved as arsine. When hydrogen ceases to be evolved, the bromine solution is boiled until free from bromine and is then returned to the solution of iron in the original flask. A condenser is now attached to the flask and the contents boiled to a low bulk. A receiver containing water is placed so that the end of the condenser dips just under the water. 25 c.c. of hydrochloric acid of sp. gr. 1·16 is now added to the flask and distillation continued, to ensure the complete expulsion of arsenic as trichloride.

According to Stead,[2] the arsenic in the distillate may be determined directly by titration, instead of being converted into magnesium pyroarsenate. The distillate is rendered alkaline with ammonia, and then slightly acidified with hydrochloric acid. A small excess of sodium bicarbonate is added, together with some starch paste, and the solution titrated with standard iodine solution. The solutions required are:—

1. Arsenious acid: 0·66 g. of pure arsenic trioxide (= 0·5 g. As) and 2 g. of sodium carbonate are dissolved in 100 c.c. of boiling water. After cooling, 2 g. of sodium bicarbonate is added and the solution made up to a litre. One c.c. = 0·5 mg. As.

2. Iodine: 1·2692 g. of resublimed iodine and 2 g. of potassium iodide are made up to a litre. One c.c. = 1 c.c. of standard arsenious acid solution = 0·5 mg. As.

Nickel.—Minute quantities of nickel occur in various classes of iron and steel. Nickel steels, however, contain from 1 to 5 per cent. of nickel but certain special steels may contain over 30 per cent.

1. *Nickel Oxide Method.* For the determination, 2 to 5 g. of iron or steel, or 1 to 3 g. of nickel steel, is dissolved in hydrochloric acid with the aid of nitric acid or potassium chlorate, evaporated to dryness, taken up with hot dilute hydrochloric acid, and filtered. An excess of ammonium chloride and ammonia are added to the filtrate, and the precipitate filtered off and redissolved, the precipitation being repeated. The united filtrates are evaporated to a small bulk, and, if necessary the ammonium salts are removed by taking to dryness and igniting.

[1] *Stahl u. Eisen*, 1889, 9, 720.

[2] *J. Iron and Steel Inst.*, 1895, i., 110; *J. Soc. Chem. Ind.*, 1895, 14, 444.

Sulphuretted hydrogen is then passed into the warm acid solution to precipitate copper, which is filtered off, the filtrate made just ammoniacal, and treated with ammonium sulphide. The combined precipitates of manganese and nickel sulphides are treated on the filter with cold dilute hydrochloric acid (1 : 6). The nickel sulphide, which remains undissolved, is thoroughly washed and ignited to NiO, which contains 78·59 per cent. nickel.

2. *Nickel Sulphide Method.* Ledebur removes the bulk of iron by means of the ether extraction method (*cf.* p. 6). The extracted solution of chlorides is then heated to expel ether, diluted, and treated with sulphuretted hydrogen to precipitate copper. After boiling off the sulphuretted hydrogen from the filtrate, it is oxidised with nitric acid, and the residual iron removed as basic ferric acetate; the nickel is then precipitated from the boiling acetic solution by sulphuretted hydrogen.

3. *Dimethylglyoxime Method.* A method, due to Tschugaeff[1] and improved by Krant[2] and Brunck,[3] which is both rapid and accurate, consists in the precipitation of nickel by means of dimethylglyoxime, $CH_3.CNOH.CNOH.CH_3$, whereby it is separated from iron chromium, zinc, manganese, and cobalt. Dimethylglyoxime is a white, crystalline powder, insoluble in water, but soluble in warm alcohol. A 1 per cent. alcoholic solution is used for the precipitation; this produces a bright red precipitate of the nickel compound, which can readily be washed, and which, when dried at 110° to 120°, has the composition $C_8H_{14}N_4O_4Ni$, and contains 20·31 per cent. Ni. A slight excess of ammonia is necessary to secure complete precipitation.

Iron, if present, is either completely oxidised to the ferric state, and the solution then treated with tartaric acid to prevent its precipitation by ammonia, or it is reduced by sulphur dioxide to the ferrous condition, and the nickel precipitated in dilute acetic acid solution in presence of sodium acetate; the former procedure is adopted in presence of chromium. Small quantities of manganese, copper, or vanadium do not influence the results; if considerable quantities of manganese are present, the precipitation must be effected in acetic acid solution.

To carry out the method, 0·5 to 1·0 g. of nickel steel is dissolved in 10 c.c. of hydrochloric acid, which should not be too concentrated, and the solution oxidised with nitric acid. From 2 to 5 g. of tartaric acid is then added, the whole diluted to 300 c.c., and a small excess of ammonia added to make sure that no precipitation occurs; the solution is then just acidified with hydrochloric acid and heated to

[1] *Z. anorg. Chem.*, 1905, **46**, 144; *Ber.*, 1905, **38**, 2520; *J. Soc. Chem. Ind.*, 1905, **24**, 941.
[2] *Z. angew. Chem.*, 1906, **19**, 1793.
[3] *Ibid.*, 1907, **20**, 834, 1844; *J. Soc. Chem. Ind.*, 1907, **26**, 643, 1217.

boiling. The precipitation of the nickel is next effected by the addition of 20 c.c. of the dimethylglyoxime solution, ammonia being subsequently added, drop by drop, to ensure complete precipitation. The precipitate can be filtered at once; but in specially accurate determinations, it is preferable to allow it to stand for twenty-four hours. The precipitate is collected either in a porcelain or platinum Gooch crucible, washed six to eight times with water, and dried at 100° to 120° till the weight is constant.

Iwanicki[1] avoids the use of a Gooch crucible by collecting the precipitate on a dried filter paper, using a similarly dried filter paper as a tare. If a hard, smooth surfaced filter paper is used, the dried precipitate may be brushed off and weighed in a tared dish. Wdowiszewski[2] converts the precipitate to nickel oxide by careful ignition; to avoid the sublimation of the glyoxime compound, the precipitate is rolled up in the moist filter paper, and then wrapped in a second filter paper before ignition.

4. *Dicyanodiamidine Method.* In this method, introduced by H. Grossmann and Schück,[3] nickel is precipitated by dicyanodiamidine sulphate. The precipitation is effected in ammoniacal solution in presence of an excess of potassium or sodium hydroxide; the precipitate is pale yellow and crystalline, and when air-dried has the composition $Ni(C_2H_5N_4O)_2 . 2H_2O$.

For the determination, from 0·5 to 2·0 g. of the sample, according to its nickel content, is dissolved in aqua regia, the solution evaporated down to 15 c.c., any separated silica filtered off, and Rochelle salt added to the filtrate to prevent the precipitation of iron; from 15 to 20 g. is added as a 50 per cent. solution for every 1 g. of iron. If much manganese is present, hydrazine sulphate is added to prevent its precipitation with the nickel. On the addition of the Rochelle salt, a precipitate of acid potassium tartrate separates, which is coloured yellow by the enclosed mother-liquor; this is dissolved by ammonia and an excess of sodium hydroxide added (50 c.c. of a 20 per cent. solution). The solution turns bright green, and should be perfectly clear. The nickel is then precipitated with 1 to 1·5 g. of dicyanodiamidine sulphate (preferably as a 10 per cent. solution), the precipitate allowed to stand for several hours, filtered off on a Gooch crucible, washed four to five times with 6 per cent. ammonia, dried at 120° to 130° and weighed. The anhydrous compound contains 22·5 per cent. of nickel.

[1] *Stahl u. Eisen*, 1908, **28**, 1547.

[2] *Stahl u. Eisen*, 1908, **28**, 960; 1909, **29**, 358; *cf.* also P. Bogoluboff, *Stahl u. Eisen*, 1910, **30**, 458; *J. Soc. Chem. Ind.*, 1910, **29**, 493.

[3] *Chem. Zeit.*, 1907, **31**, 535, 911; *Stahl u. Eisen*, 1909, **29**, 143; *cf.* also Prettner, *Chem. Zeit.*, 1909, **36**, 396, 411; *J. Soc. Chem. Ind.*, 1909, **28**, 525.

5. *Potassium Cyanide Volumetric Method.* The following rapid method of determining the percentage of nickel in nickel steels is employed in many laboratories.[1]

One gram of the sample is dissolved to a clear solution in 20 c.c. of nitric acid (1 : 1), the nitrous fumes boiled off, 100 c.c. of distilled water added, and the solution allowed to cool. Fifteen c.c. of ammonium citrate solution (225 g. citric acid, 450 c.c. strong ammonia, and 150 c.c. water) is added, the whole neutralised with strong ammonia, and when quite neutral, not more than 1 c.c. of ammonia added in excess. A crystal of potassium iodide is then stirred in and the solution titrated with a solution of potassium cyanide containing silver nitrate (12·5 g. potassium cyanide, 0·25 g. silver nitrate, and 2000 c.c. water). The opalescence produced by the first additions of the cyanide solution is cleared up by further addition of cyanide until the solution remains crystal-clear for at least three minutes. The cyanide solution is standardised against a known nickel steel or against 30 mg. of pure electrolytic nickel, which represents 1 g. of steel containing about 3·0 per cent. of nickel. The strength of the cyanide solution is so adjusted that approximately 30 c.c. are used for 30 mg. of nickel.

This method is equally applicable for steels in sulphuric acid solution. In fact the presence of ammonium sulphate in the solution is desirable, as it increases the delicacy of the end reaction. A variation of this method, which has the advantage of permitting a repetition of the end-point should it be overshot, is conducted as follows: 0·5 to 1 g. of the steel is dissolved in hydrochloric acid, oxidised with nitric acid, and most of the acid evaporated off. The residue is dissolved in a little water and about 20 g. of citric acid added. When this has dissolved, the liquid is neutralised with ammonia and 1 c.c. added in excess. The neutralisation is best finished in the cold. Two c.c. of silver nitrate solution (5 g. per litre) is then added accurately from a burette to the cold liquid, followed by 30 c.c. of a solution containing about 400 g. ammonium sulphate and 20 g. potassium iodide per litre. The solution is then titrated with potassium cyanide until the turbidity just disappears. If necessary it can be restored by further addition of silver nitrate and the end-point repeated. The silver nitrate solution is titrated against the cyanide and the volume of cyanide equivalent to the silver nitrate used is deducted from the burette reading. The observation of the end-point of this reaction is much facilitated by the use of a box with two compartments side by side; one of them, lined with black, is provided with a hole for insertion of the beaker and the other contains an electric lamp from which a beam of light is projected through a hole in the

[1] *Cf.* G. T. Dougherty, *Chem. News*, 1907, **95**, 261, 268; and C. M. Johnson, *J. Amer. Chem. Soc.*, 1907, **29**, 1201.

partition, illuminating the solution and making the slightest turbidity apparent.

Steels containing much chromium give a very dark coloured citrate solution, which can be lightened somewhat by increasing the amount of citric acid used, but the following procedure overcomes this difficulty entirely. The steel is dissolved in nitric acid of sp. gr. 1·2, and the solution neutralised with ammonia as completely as possible without the production of a permanent precipitate. After cooling, a volume of potassium cyanide solution is added, which is judged to be somewhat in excess of the amount required by the nickel in the sample. Sufficient dilute ammonia (10 c.c. of 1 : 1), to precipitate the whole of the iron, chromium, etc., is added, the solution made up to a definite volume, filtered, and half the volume collected. This filtrate, after addition of the ammonium sulphate and potassium iodide indicator, is titrated with silver nitrate until a turbidity just appears.

6. *Electrolytic Method.* Neumann[1] has worked out the following electrolytic method for the determination of nickel in nickel steel. From 2·5 to 5 g. of the metal is dissolved in dilute sulphuric acid, the solution oxidised with hydrogen peroxide and ammonium sulphate, and an excess of ammonia added. The liquid is boiled, thoroughly shaken, allowed to cool, and made up to 500 c.c. The precipitated iron is then filtered off and 100 c.c. of the clear solution withdrawn by a pipette, or separated by filtration through a dry filter paper, for electrolysis. Ammonium sulphate is added until the total quantity reaches 10 g., and in addition, 30 to 40 c.c. of ammonia and 20 to 60 c.c. of water. An electromotive force of 3½ to 4 volts, and a current density of 1 to 2 ampères per square decimetre, is used for the electrolysis, the liquid being warmed to 50° to 60°. The time required is about two hours. The accuracy of the method is not affected by the presence of silicon, carbon, or chromium, provided the last is not present as chromic acid. Manganese is, at most, deposited in traces with the nickel, but cobalt if present is deposited.

Cobalt.—Cobalt is an important constituent of certain magnet steels and is also a constituent of some varieties of tool steel, generally in association with considerable quantities of chromium. After treatment with the ordinary acid mixtures, the latter class of steels leave residues which may need very prolonged digestion for their complete solution, and time can be saved by filtering off the residue and fusing with alkali carbonates, adding the acidified solution from the fusion to the original filtrate.

For the determination of cobalt (and nickel) the iron and chromium are most conveniently removed by the basic acetate method (p. 7). The filtrate, after boiling down, is neutralised with acetic acid, about

[1] *Stahl u. Eisen*, 1898, **18**, 910 ; *J. Soc. Chem. Ind.*, 1898, **17**, 1074.

5 c.c. added in excess together with 20 c.c. ammonium acetate, and thoroughly saturated with hydrogen sulphide while hot. The precipitate of nickel and cobalt sulphides is filtered, washed, ignited at a moderate red heat (800° to 900°), and weighed as $NiO + Co_3O_4$. The filtrate should be again boiled and treated with hydrogen sulphide to ensure complete precipitation. The nickel may be determined in a separate portion of the steel, or in the weighed oxides by means of dimethylglyoxime (p. 66) and the cobalt obtained by difference, or the latter may be directly separated from the mixture by the method of Ilinski and Knorre.[1] In this process the cobalt is precipitated from a warm solution containing 5 to 10 per cent. of hydrochloric acid, by adding an excess of a solution of nitroso-β-naphthol prepared by dissolving 2 g. of the solid in 75 c.c. glacial acetic acid and diluting to 150 c.c. with water. After digesting for about an hour, the dark red precipitate is filtered, washed first with 5 per cent. hydrochloric acid, then with water and ignited in a muffle at 800° to Co_3O_4 which contains 73·44 per cent. of cobalt.

Cobalt may also be determined by precipitation as cobalt ammonium phosphate.[2] Manganese if present is precipitated with the cobalt and should be separately determined and allowed for. If nickel is also present, this should be precipitated from the basic acetate filtrate by means of dimethylglyoxime, and the excess of this reagent decomposed by means of nitric acid. The solution is then neutralised with ammonia, made very slightly acid with hydrochloric acid, heated nearly to boiling and treated with 10 to 20 c.c. of a saturated solution of sodium phosphate. Ammonia is then added in drops until the solution is just alkaline and the mixture is digested and stirred until the precipitate becomes pink and densely crystalline. It is then filtered on paper pulp, washed with hot water, ignited, and weighed as $Co_2P_2O_7$. The pulp should be wrapped in a wet filter paper and the ignition conducted with care to avoid mechanical loss.

Chromium.—Chrome steels with low chromium content are soluble in sulphuric acid, hydrochloric acid, or aqua regia. Ferro-chrome and steels with a high percentage of chromium, however, are resistant towards acid, and have to be treated by fusion.

Ziegler[3] fuses 0·5 g. of ferro-chrome in a silver crucible with 6 g. of sodium hydroxide and 3 g. of nitre. The charge is heated up very gradually, so as to reach complete fusion in half an hour. The melt is taken up with water, saturated with carbon dioxide, evaporated to dryness, lixiviated, filtered, and the residue washed with water containing sodium carbonate. By this procedure an efficient separation

[1] *Ber.*, 1885, **18**, 699.
[2] *Cf.* L. Dufty, *J. Iron and Steel Inst.*, 1914, ii., 52.
[3] *Dingl. polyt. J.*, 1889, **274**, 513; *Chem. News*, 1892, **66**, 295.

of iron and chromium is usually attained; it is desirable, however, to test the ferric residue, both for unattacked metal and for chromium.

Namias[1] fuses 1 g. of ferro-chrome with 8 to 10 g. of acid potassium sulphate; after fusing for one hour, 2 to 3 g. more of acid sulphate is added and fused. The mass is dissolved in dilute hydrochloric acid, the silica filtered off, the filtrate nearly neutralised with sodium hydroxide, and precipitated by means of 2 g. of magnesia suspended in water. The precipitate is filtered, washed, ignited, and fused with a mixture of sodium carbonate and nitrate; all the chromium is thus ultimately obtained as sodium chromate.

Spüller and Brenner[2] mix 0·35 g. of finely ground ferro-chrome with 2 g. of dry powdered sodium hydroxide, with a silver spatula in a silver crucible, and cover the mixture with a layer of 4 g. of sodium peroxide. The mixture is rapidly heated to incipient fusion; the burner is withdrawn during the violent reaction which occurs. After the first reaction is over the mass is fused for ten minutes, 5 g. of sodium peroxide carefully stirred in, the fusion continued for thirty minutes, a further 5 g. of peroxide added, and the mass again ignited for twenty minutes; the oxidation should then be complete. Finally, another 5 g. of peroxide is incorporated, in order to facilitate the lixiviation, and the crucible immediately allowed to cool. The further procedure is the same as for chromiferous ores (*cf.* pp. 12, 33).

In the analysis of chrome steel, 2 g. is dissolved in 20 c.c. of strong hydrochloric acid and the solution evaporated to dryness with 10 c.c. of sulphuric acid (1 : 1). The residue is heated to expel excess of acid. transferred to a silver crucible, and then treated like ferro-chrome.

In dealing with pig iron containing very little chromium, Donath[3] proceeds as follows:—Three grams of metal is dissolved in hydrochloric acid (1 : 1) and the solution heated to boiling. Meanwhile a solution of sodium carbonate is heated up in a porcelain dish. Both solutions are tinged a full red by the addition of potassium permanganate. The iron solution is then slowly run into the sodium carbonate; the iron and manganese are precipitated, while the chromium remains in solution as sodium chromate. The excess of permanganate is decomposed by alcohol, and the filtrate is then ready for the determination of the chromium.

Stead[4] separates chromium from iron by precipitation as phosphate from a neutral solution in presence of sodium thiosulphate and acetate as in the method described on p. 82 for aluminium, fuses the precipitate with magnesia and sodium hydroxide, and so obtains sodium chromate.

[1] *Stahl u. Eisen*, 1890, **10**, 977; *J. Iron and Steel Inst.*, 1890, ii., 853.
[2] *Chem. Zeit.*, 1897, **21**, 3; *Stahl u. Eisen*, 1897, **17**, 101.
[3] *Stahl u. Eisen*, 1894, **14**, 446; *J. Iron and Steel Inst.*, 1894, ii., 493.
[4] *J. Iron and Steel Inst.*, 1893, i., 160.

When the chromiferous metal is soluble in acids, it is generally advantageous to remove the bulk of the iron by extraction with ether (*cf.* p. 6).

The gravimetric determination of chromium in sodium chromate solutions is carried out as described under the analysis of ores (p. 12).

To determine chromium volumetrically, a solution of 14 g. of ferrous ammonium sulphate in 1 litre of water, standardised against decinormal potassium permanganate or bichromate, is used. The chromate solution is diluted, acidified with sulphuric acid, and reduced with the ferrous solution, the excess of which is titrated back with permanganate or bichromate. The iron value of the solution, multiplied by 0.3109 $\left(\frac{52\cdot12}{167\cdot64}\right)$, gives the value for chromium, since 3 g.-mol. of ferrous ammonium sulphate is oxidised by one equivalent of chromium. When the chromium is very small in amount, it is preferable, according to Zulkowski,[1] to titrate with potassium iodide and standard sodium thiosulphate, a check determination being carried out simultaneously with a known quantity of a standard potassium bichromate solution. The solution of the chromate corresponding to 1 g. of the sample is treated with 10 c.c. of potassium iodide solution (1 : 10), hydrochloric acid of sp. gr. 1·12 added, and the liberated iodine titrated with sodium thiosulphate after standing for fifteen minutes in the dark. Twenty c.c. of a potassium bichromate solution, containing 0·9918 g. $K_2Cr_2O_7$ per litre = 0·00695 g. Cr per 20 c.c., is similarly titrated. The sodium thiosulphate solution contains 4·966 g. $Na_2S_2O_3 \cdot 5\,H_2O$ per litre.

Schneider[2] dissolves 2 g. of chrome steel in dilute sulphuric acid, oxidises with 5 c.c. of strong nitric acid, boils off the nitrous fumes adds 5 g. of lead peroxide, boils again for a quarter of an hour, and filters. The filtrate is rendered ammoniacal, and boiled for a short time till the permanganate formed is decomposed. Sulphuric acid is then added to dissolve the precipitate and the solution (filtered if necessary) titrated as above, after dilution to 1 litre. Should the solution, after the precipitation of iron, be so poor in chromium (less than 0·1 per cent.) as not to appear yellow, it is separated by partial filtration, the filtrate acidified with sulphuric acid, and titrated.

The lead peroxide used in the foregoing method may be replaced by potassium permanganate, a strong solution of which is added drop by drop to the boiling solution of the steel until a permanent dark brown precipitate of manganese dioxide is produced. Should a permanganate coloration persist after boiling for a few minutes, it may be removed by the cautious addition of a few drops of manganese

[1] *Chem. Zeit.*, 1897, 21, 3 ; *Stahl u. Eisen*, 1897, 17, 101.
[2] *Oesterr. Zeitschrift*, 40, 235 ; *J. Iron and Steel Inst.*, 1892, ii., 515.

sulphate solution, but it is desirable to avoid this if possible as a large precipitate of manganese dioxide is difficult to wash free from chromium. The solution is filtered through asbestos, cooled and titrated with ferrous sulphate. In the Stead process, filtration is obviated by boiling with dilute hydrochloric acid until the manganese dioxide is dissolved, then diluting and boiling until chlorine is completely expelled.

The following volumetric methods for the determination of chromium in iron and steel are due to A. W. Gregory and J. MacCallum.[1] Two grams of the metal is dissolved in as little nitric acid as possible and silver nitrate and ammonium persulphate added; after boiling, ammonium chloride is added in sufficient quantity to precipitate nearly all the silver, the solution diluted to a definite volume, and filtered through asbestos. A quantity of the filtrate equal to half the original volume of the solution is taken, excess of standard ferrous sulphate solution added to reduce the chromate which has been formed, and the excess of ferrous sulphate determined by titration with standard potassium bichromate solution.

Chromium can also be determined by means of sodium bismuthate, Two grams of the steel is dissolved in nitric acid, and about 3 g. of bismuthate added in small quantities at a time; the solution is boiled till all the manganese is precipitated as dioxide, enough very dilute hydrochloric acid added to dissolve the manganese dioxide, and then excess of silver nitrate. The solution is boiled, made up to a definite volume, filtered through asbestos, and an aliquot portion titrated with ferrous sulphate and bichromate as above.

A colorimetric method for the estimation of chromium has been described by Hillebrand.[2]

Tungsten.—Tungsten steel and ferro-tungsten are soluble in acids, whereas metallic tungsten is almost insoluble. All methods of analysis are based upon the separation of tungstic acid, which is purified and weighed as tungsten trioxide.

In the analysis of tungsten steel, 1 to 2 g. is dissolved in dilute nitric acid and the solution evaporated down with sulphuric acid, as in the determination of silicon by Drown's method (p. 51). The insoluble residue obtained on lixiviation is treated with hydrofluoric acid to expel silica, and ignited, but not over the blow-pipe. The trioxide is always contaminated with iron. According to Auchy,[3] the amount of this impurity is practically constant, viz., from 0·02 to 0·03 per cent. for steels containing less than 1 per cent. of tungsten, and from 0·03 to

[1] *J. Chem. Soc.*, 1907, **91**, 1846. *Cf.* also G. v. Knorre, *Stahl u. Eisen*, 1907, **27**, 1251, and Phillips. *Ibid.*, 1907, **27**, 1164.

[2] *J. Amer. Chem. Soc.*, 1898, **20**, 454; *Chem. News*, 1898, **78**, 227.

[3] *J. Amer. Chem. Soc.*, 1899, **21**, 239; *J. Chem. Soc.*, 1899, **76**, 524.

0·04 per cent. for those which contain a higher proportion; it cannot be removed by washing with hydrochloric acid. In order to obtain perfectly pure trioxide, the impure substance is converted into sodium tungstate by fusion with sodium carbonate, the melt lixiviated, the solution evaporated to dryness with nitric acid, and extracted with water; the trioxide thus left behind is filtered off, washed with dilute ammonium nitrate solution, dissolved in ammonia, evaporated to dryness in a platinum vessel, and ignited and weighed. For ordinary purposes it is sufficiently accurate to deduct from the weight of the ignited impure tungstic oxide the amount of insoluble residue obtained by lixiviating the sodium carbonate fusion.

Herting[1] determines tungstic acid volumetrically by titration with sodium hydroxide. The precipitated acid, still contaminated with silica and iron, is washed on the filter with dilute nitric acid and then with 5 to 10 per cent. potassium nitrate until the filtrate is neutral. It is then rinsed into a flask, boiled with 200 c.c. of water, and titrated whilst hot with $N/1$ sodium hydroxide, phenolphthalein being employed as indicator. One c.c. of sodium hydroxide solution neutralises 0·116 g. of WO_3, equivalent to 0·092 g. of tungsten.

Ferro-tungsten dissolves readily in aqua regia, but as some of the metal may escape attack through being coated with tungstic acid, it is better to decompose by fusion. Alkali carbonate and nitre, or sodium hydroxide and peroxide, or acid potassium sulphate, or a mixture of three parts of fusion mixture with two parts of anhydrous borax, may be used for this fusion.

Metallic tungsten is converted into the trioxide by roasting, either alone (Preusser[2]) or with ammonium nitrate (Ziegler[3]). This is then further converted into sodium tungstate, either in the wet or dry way, and the clear solution evaporated with nitric acid, as above.

Tungstic acid is readily precipitated from alkaline solutions such as result from fusion by means of mercurous nitrate. The solution must be carefully neutralised with nitric acid and treated with dilute mercurous nitrate solution, which should be only slightly acid, until precipitation appears to be complete. The free nitric acid must then be completely neutralised by stirring with excess of mercuric oxide emulsion. The ignited precipitate containing all the tungstic oxide should be examined for impurities such as silica and chromic oxide.

Both metallic tungsten and ferro-tungsten are readily attacked by warming with hydrofluoric acid in a platinum dish and cautiously adding nitric acid until no further action ensues. The solution is then

[1] *Z. angew. Chem.*, 1901, 14, 165.
[2] *Z. anal. Chem.*, 1889, 29, 173; *Chem. News*, 1889, 60, 37.
[3] *Chem. Zeit.*, 1889, 13, 1060; *Chem. News*, 1889, 60, 272.

evaporated with sulphuric acid till fumes are evolved, the residue boiled with dilute hydrochloric acid, and the insoluble tungstic acid treated in the usual manner.

A method for dissolving ferro-tungsten, proposed by Namias,[1] consists in boiling the finely powdered alloy with concentrated sodium hydroxide or carbonate solution to which bromine has been added.

Molybdenum.—This element is present in molybdenum steels and in ferro-molybdenum used in the manufacture of the steel. It may be determined by oxidising to molybdic acid, separating from iron, reducing to Mo_2O_3, and titrating with potassium permanganate.[2]

Convenient quantities for analysis are 1·5 g. of steel or 0·3 g. of ferro-molybdenum. The metal is dissolved in nitric acid, with or without addition of potassium chlorate, evaporated to dryness, redissolved in 20 c.c. of hydrochloric acid of sp. gr. 1·19, again evaporated to dryness, and taken up with 10 c.c. of hydrochloric acid. The solution is run in a thin stream into 100 c.c. of boiling 10 per cent. sodium hydroxide solution, which is then transferred to a 300 c.c. measuring flask, made up to the mark, and thoroughly shaken. It is then filtered through a dry filter paper into a capacious flask, and 200 c.c. of the clear filtrate treated with 80 c.c. of hot dilute sulphuric acid (1 : 4) and 10 g. of zinc, and the liquid warmed, without actually boiling, for twenty to twenty-five minutes, until the reduction is complete. It is then rapidly freed from zinc by filtration and titrated with $N/10$ or $N/20$ potassium permanganate. The iron value of the permanganate, multiplied by 0·606, gives the molybdenum.

The reduced molybdenum solution is readily oxidised by exposure to the atmosphere, and a more satisfactory means of carrying out the determination is afforded by the use of the Jones reductor. This consists of a wide burette tube provided with a funnel top. A layer of ignited asbestos is placed on a filter plate immediately above the stopcock and the rest of the tube is filled with amalgamated zinc granules of approximately 0·05 cm. diameter. The zinc is amalgamated with about 1 per cent. of its weight of mercury by shaking with a dilute mercuric sulphate solution of suitable strength. After washing with water it is lightly packed in the reductor tube and kept covered with water while not in use. The lower end of the reductor is connected to a receiver, such as a filter flask to which suction can be applied, and the receiver is charged with a solution containing a moderate excess of ferric ammonium sulphate in 2½ per cent. sulphuric acid, into which the delivery tube of the reductor dips. A determination is performed by first passing about 100 c.c. of 2½ per cent. sulphuric acid through the tube, then the molybdenum solution containing a similar

[1] *Stahl u. Eisen*, 1891, **11**, 757 ; *J. Chem. Soc.*, 1892, **62**, 539.

[2] Auchy, *J. Amer. Chem. Soc.*, 1902, **24**, 273 ; 1903, **25**, 215.

amount of acid and warmed to about 30°, followed by 100 c.c. more of dilute acid, and finally about 100 c.c. water. The rate of flow should be adjusted to allow the passage of 100 c.c. in ten to twenty minutes. The reduced molybdenum solution reacts at once with the ferric sulphate in the receiver, producing ferrous sulphate which is titrated with permanganate.

A gravimetric determination of molybdenum can be made, after separating the iron with sodium hydroxide as for the preceding method, by acidifying the alkaline filtrate with hydrochloric acid and adding excess of lead acetate to the boiling solution, followed by sufficient ammonium acetate to react with any free hydrochloric acid. The precipitate is filtered, washed with hot water, ignited, and weighed as $PbMoO_4$.

Molybdenum may also be determined in steels by precipitation as sulphide, without the preliminary separation of the iron. This is best accomplished in solutions containing about 5 per cent. of free sulphuric acid, and is aided, especially when dealing with large quantities, by heating the solution in a closed flask, on the water bath, after saturating with hydrogen sulphide.

For determining the small quantities usually found in steel, the following procedure will be found to be satisfactory. Two grams of the steel is dissolved in hydrochloric acid, oxidised with a little nitric acid, evaporated to a syrup and diluted, a little hydrochloric acid being added if necessary. Any silica and tungstic acid which may be present is filtered off. The filtrate is neutralised with sodium hydroxide and sufficient sulphuric acid is added to give a concentration of 4 or 5 per cent.; the solution is heated to boiling and a rapid stream of hydrogen sulphide passed until the solution is nearly cold. Treatment with hydrogen sulphide under pressure gives a precipitate which is easily filtered. The precipitate of mixed sulphur and molybdenum sulphide should separate clearly. It is filtered on paper pulp, washed with cold 2 per cent. sulphuric acid, and ignited carefully until the sulphide is converted into the white oxide MoO_3. The temperature of ignition must not be allowed to exceed dull redness, otherwise loss by volatilisation will occur. After weighing, the oxide should be fused with a little sodium carbonate, extracted with water, and the residue consisting of ferric oxide and possibly copper oxide, weighed and deducted from the initial weight after calculating to sulphides. Instead of weighing and deducting this residue, the molybdenum may be precipitated as lead molybdate from the extract of the fusion by the method described above.

These methods are not suitable when vanadium is present, in which case the method described under vanadium (p. 79) is used.

Vanadium.—This element occurs as an ingredient of vanadium steel and of many high speed tool steels.

1. *Gravimetric Method.* For the determination of traces of vanadium in steel, 50 g. of the sample is dissolved in very dilute sulphuric acid (1 : 20); the acid is preferably mixed and cooled before using, and then allowed to act on the metal overnight. The carbonaceous residue is collected on a filter, transferred while wet to a platinum dish, dried, ignited, and allowed to cool. The residue is thoroughly mixed with sodium carbonate and a few crystals of finely crushed potassium permanganate, fused for some minutes, extracted with boiling water, filtered, and dilute nitric acid added to the filtrate till just on the point of acidity; a few drops of sodium carbonate are then added, and the solution filtered from any small quantities of iron and manganese or silica that are precipitated. The filtrate is made slightly acid and the vanadium precipitated by mercurous nitrate, with the addition of mercuric oxide to ensure the neutrality of the solution.

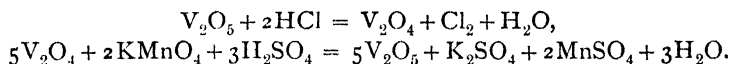
The mercury precipitate obtained by boiling the solution contains, besides the vanadium, any tungsten, chromium, or molybdenum that may have been present in the sample. The residue, after ignition of the mercury precipitate, is again fused with a little sodium carbonate and a little nitrate, and extracted with the minimum quantity of water. From this solution the vanadium is precipitated by saturating the solution with pure solid ammonium chloride. After a few hours, the separated vanadium is collected, washed with ammonium chloride solution, ignited, and weighed as the pentoxide, V_2O_5 (Lambert).

2. *Volumetric Methods.* The following volumetric method for the determination of vanadium, due to E. Campagne,[1] is to be recommended in absence of chromium, or if only an inconsiderable quantity of this metal is present. From 2·5 to 5·0 g. of the sample, according to its content of vanadium, is dissolved in 60 c.c. of nitric acid of sp. gr. 1·18, and the solution evaporated to dryness in a porcelain dish; if the alloy is rich in vanadium, 0·25 g. is taken and dissolved in 20 c.c. of acid. The residue is heated to decompose the nitrates (as in the determination of phosphorus), dissolved in concentrated hydrochloric acid, the bulk of the iron removed by the ether extraction process, the residual liquor evaporated twice successively almost to dryness, taken up with 50 c.c. of concentrated hydrochloric acid, and finally again evaporated with 5 to 10 c.c. of concentrated sulphuric acid until acid fumes begin to be evolved. The liquid is then allowed to cool, dissolved in 300 c.c. of water, warmed to about 60°, and titrated with dilute permanganate solution.

The vanadic acid initially formed is reduced by the hydrochloric

[1] *Ber.*, 1903, 36, 3166.

acid, and the lower oxide then oxidised by the permanganate in accordance with the following equations:—

$$V_2O_5 + 2HCl = V_2O_4 + Cl_2 + H_2O,$$
$$5V_2O_4 + 2KMnO_4 + 3H_2SO_4 = 5V_2O_5 + K_2SO_4 + 2MnSO_4 + 3H_2O.$$

The iron value of the permanganate solution, multiplied by 0·914, gives the value for vanadium; it is advisable to dilute the permanganate solution to five times its volume, on account of the small proportions of vanadium usually present; the conversion factor is then 0·1828.

A convenient volumetric process for ferro-vanadium is the following: Half a gram is dissolved in 20 c.c. dilute sulphuric acid (1 to 5), oxidised with a little nitric acid, and boiled with a little permanganate to destroy carbonaceous matter. The precipitate of manganic oxide is dissolved with a few drops of ferrous sulphate and the solution cooled. Permanganate is added in drops until a faint pink colour persists, showing that the vanadium is fully oxidised. Standard ferrous ammonium sulphate is now run in until a spot test with ferricyanide gives an immediate blue colour. The end-point may be repeated by adding a little more ferrous solution followed by standard permanganate until no immediate blue colour is produced with a ferricyanide spot test. The vanadium is equivalent to the difference between the total amounts of ferrous solution and permanganate consumed. One c.c. *N*/10 solution = 0·0051 g. vanadium. As the solution finally contains only reduced vanadium with no excess of ferrous sulphate, the determination may be confirmed by warming to about 70°, and titrating with permanganate until a permanent pink colour appears.[1]

In steels, vanadium is usually associated with chromium, frequently in comparatively large amounts, and it is desirable to separate the chromium as well as the iron before attempting a vanadium determination. For this purpose, 2 or 3 g. is dissolved and treated by the ether separation process, as described on p. 6. The acid solution, after boiling off the ether, is evaporated with 10 c.c. nitric acid until syrupy, and diluted with a little water. The solution should be more or less blue according to the amount of chromium present. If it is green or yellowish on account of the presence of chromic acid, weak sulphurous acid is added in drops until no further colour change occurs, but any excess must be avoided. The solution is now run slowly into 100 c.c. of boiling 10 per cent. sodium hydroxide solution. The precipitated hydroxides of iron, chromium, manganese, nickel, etc., are filtered off, and, if at all bulky, dissolved in a little dilute nitric acid and reprecipitated in a similar manner. The combined filtrates are acidified with nitric acid, again cautiously reduced with sulphurous acid if any

[1] See also K. Someya, *Sci. Rep. Tōhoku*, 1925, **14**, 577; *J. Soc. Chem. Ind.*, 1926, **45**, B. 278.

chromic acid colour is apparent, and made just alkaline with sodium hydroxide. The further slight precipitate of chromium hydroxide usually obtained is filtered off, and the vanadium precipitated from the filtrate by adding lead acetate and an excess of acetic acid.

When vanadium and molybdenum are present together, they may be determined in the following manner: The steel is dissolved and tungsten and silica separated in the usual way. The filtrate is concentrated, partly neutralised with sodium hydroxide and run into excess of boiling sodium hydroxide solution, as described under molybdenum (p. 75). The ferric hydroxide precipitate, which still contains a little vanadium, is redissolved and the sodium hydroxide separation repeated. The combined alkaline filtrates are acidified with hydrochloric acid and boiled for a minute or so. Any chromium that may have been oxidised during the separation should be reduced at this stage by cautious additions of sulphurous acid. After cooling, a little permanganate is added to oxidise the vanadium, then excess of lead acetate and 30 c.c. of ammonium acetate and the whole heated to boiling. The precipitate of lead vanadate and molybdate is filtered, washed, and ignited gently. The ignited residue is dissolved in hydrochloric acid, evaporated with 5 c.c. sulphuric acid, cooled, diluted and the lead sulphate is filtered off. The vanadium is determined by reducing the solution with sulphurous acid, boiling off the excess, and titrating with permanganate at about 70°. The acidity of the solution is afterwards adjusted to about 2·5 per cent., and the liquid, after cooling to about 30°, is passed through the Jones reductor into ferric alum, as described under molybdenum, and again titrated with permanganate, at first cold and finally at about 70°. Since, in the reductor the vanadium is reduced to hypovanadious oxide, V_2O_2, it will absorb three times as much permanganate in the second titration as in the first in which the change is from V_2O_4 to V_2O_5: hence, to obtain the molybdenum, it is necessary to deduct from the second titration three times the volume used in the first one.

3. *Colorimetric Method.* One gram of the sample and 1 g. of a steel free from vanadium and approximately of the same carbon content are dissolved in equal quantities of dilute nitric acid. Potassium permanganate solution is added to each until manganese dioxide is precipitated and persists on boiling. The solutions are cleared by the addition of sulphurous acid and then boiled to expel the excess of sulphur dioxide. Each solution is now diluted to the same volume and permanganate added very carefully, until one drop gives a permanent pink colour. Ten c.c. of hydrogen peroxide is now added to each, and the brown colour developed in the vanadium steel solution is matched by running in standard vanadium solution from a burette into the solution of the steel free from vanadium. As the vanadium

solution is run in, water is added to the vanadium steel solution in order to maintain the same volume in each.

Titanium.[1]—Titaniferous ores generally yield pig iron containing this metal; refined iron and steel, however, are generally free from it. Ferro-titanium alloys are prepared for special purposes.

The older method of determining titanium is based on the precipitation of titanium dioxide from solutions in sulphuric acid by prolonged boiling. For pig iron, 5 to 10 g. of the metal is dissolved in hydrochloric acid, evaporated to complete dryness, taken up with dilute acid, and filtered. The insoluble residue is ignited, evaporated with hydrofluoric acid and a little sulphuric acid, and fused with acid potassium sulphate. The melt is dissolved in cold water and added to the ferric chloride solution, which is then evaporated down with sulphuric acid until all the hydrochloric acid is expelled; the residue is taken up with water, and reduced by means of sulphur dioxide or sodium sulphite. The solution thus obtained is nearly neutralised with sodium carbonate and boiled in a covered beaker for two hours, the vaporised water and sulphurous acid being replaced from time to time. Titanium dioxide and a little iron as phosphate are thus thrown down and filtered off. The precipitate is fused with sodium nitrate and carbonate, and the melt extracted with water, which leaves sodium titanate and ferric oxide undissolved, whilst the sodium phosphate goes into solution. The residue is dissolved in sulphuric acid, reduced, and boiled as before. The titanium now comes down as a pure white precipitate, and is filtered off, ignited, and weighed. Ignition with ammonium carbonate ensures complete removal of sulphuric acid. According to Baskerville,[2] titanium dioxide is precipitated from a neutral ferric chloride solution on boiling, after reduction with sulphur dioxide.

Ledebur[3] found that a large excess of iron chloride prevents the titanium from being completely precipitated; to overcome this, he adopted the following method of determination. The silica having been rendered insoluble by evaporation to dryness, the residue is taken up with dilute hydrochloric acid, and the filtered solution, after concentration, is twice treated with ether (*cf.* p. 6). The resulting aqueous solutions, from which titanium may already have begun to settle out, are united and evaporated to dryness; when the residue is taken up with dilute hydrochloric acid, titanium dioxide, in a pure condition, remains undissolved. This method is less tedious than the above.

The method most frequently adopted in technical laboratories consists in dissolving about 5 g. of the sample in hydrochloric acid,

[1] *Titanium, with special reference to the Analysis of Titaniferous Substances*, by W. H. Thornton. Chemical Catalog Co.

[2] *J. Amer. Chem. Soc.*, 1894, 16, 427. [3] *Stahl u. Eisen*, 1894, 14, 810.

and, when hydrogen is no longer evolved, diluting to about 250 c.c. with water. The solution is then rendered neutral with ammonia, any traces of iron being dissolved by the addition of a drop or two of dilute hydrochloric acid. Ten to twelve grams of sodium thiosulphate is then added and the whole gently boiled on a hot plate for twenty minutes. The precipitate is filtered, washed with 3 per cent. acetic acid, and ignited to TiO_2. If necessary, the ignited precipitate is then purified after treatment with hydrofluoric and sulphuric acids, by fusion and reprecipitation, or the titanium is estimated colorimetrically.

Titanium dioxide, when free from iron, is conveniently estimated colorimetrically by the orange colour given with hydrogen peroxide in sulphuric acid solution. The standard is prepared by adding to a solution containing 1 mg. of TiO_2 per c.c. an equal volume of hydrogen peroxide, so that the resulting liquid contains 0·5 mg. per c.c. Schneider[1] proposes to determine titanium before precipitating the aluminium (*cf.* p. 83). The iron is removed by means of ammonium sulphide, the filtrate evaporated to dryness, fused with sodium carbonate, and taken up with sulphuric acid; the titanium is then estimated colorimetrically in this solution.

The application of this method is, however, somewhat limited, as molybdenum, vanadium, chromium, nickel, copper, and fluorides interfere with the colorimetric estimation of the titanium.

When pig irons are decomposed by means of nitric acid of 1·2 sp. gr., the residue of graphite, etc., is practically free from titanium, so that after filtering, the solution may be used directly for the colorimetric determination.

Ferro-titanium does not dissolve readily in acids. It may be decomposed by distributing 0·5 g. of the finely divided alloy upon the surface of 10 g. of acid potassium sulphate fused and cooled in a large platinum crucible. The contents of the crucible are then heated and the temperature maintained "until no gritty particles can be felt with a stout platinum wire" (Brearley and Ibbotson). The mass, when cold, is digested with water. Ten c.c. of sulphuric acid is then added and the solution gently heated until everything but silica has dissolved. The titanium is precipitated from the filtered solution by boiling with sodium thiosulphate.

G. W. Wdowischewski[2] has proposed the following method for the determination of titanium in ferro-titanium. The alloy is dissolved in moderately dilute sulphuric acid, the solution treated with nitric acid, and after filtering off the silica, tartaric acid and ammonia are added. The iron is then precipitated with hydrogen sulphide, filtered off, the

[1] *Oesterr. Zeitschrift*, 40, 471; *J. Iron and Steel Inst.*, 1892, ii., 517.
[2] *Eng. and Min. J.*, 1908, 85, 1200.

tartaric acid in the filtrate decomposed by addition of more nitric acid, followed by heating, and then ammonia added to the colourless solution, when the titanic acid is precipitated in the form of white flakes free from iron.

A convenient precipitant for titanium is "cupferron," which can be used in strongly acid solutions and provides a simple means for the separation of titanium from aluminium. Cupferron,[1] originally introduced by Baudisch,[2] is the ammonium salt of nitrosophenyl hydroxylamine. It is soluble in water and is used as a 6 per cent. solution, which should be freshly made for each determination. The titanium solution should be free from copper and iron, as the reagent also precipitates these metals. To the cold sulphuric acid solution of titanium, obtained by any of the foregoing methods, the cupferron solution is added slowly with continuous stirring, until after the yellow titanium compound has settled, a further addition of the reagent produces only a white precipitate of the free base. The precipitate is then filtered on paper pulp, washed well with 10 per cent. hydrochloric acid, ignited at first cautiously, then strongly, and the residue weighed as TiO_2.

Aluminium.—Aluminium may be present up to 10 per cent. as a constituent of ferro-aluminium, or in very small quantity in steel, to which it has been added as a deoxidiser. The analysis of ferro-aluminium is perfectly straightforward. It dissolves readily in acids, and the further procedure is the same as for argillaceous iron ores (*cf.* p. 5). The determination of small quantities of aluminium in presence of much iron, on the other hand, is somewhat difficult if the ordinary methods of analysis are used; it is, however, much facilitated by the use of the ether extraction method (p. 6) for the removal of the bulk of the iron.

According to Carnot,[3] aluminium is precipitated completely as phosphate from dilute acetic acid solution on boiling, even in presence of a large excess of iron, provided the latter is in the ferrous condition. To carry out the determination, 10 g. of metal is dissolved in hydrochloric acid and neutralised, first with ammonia and finally with sodium carbonate. Sodium thiosulphate is added until the solution is colourless, then 2 to 3 c.c. of a saturated sodium phosphate solution and 20 c.c. of sodium acetate solution, and the liquid boiled for three-quarters of an hour; the smell of sulphur dioxide should be no longer noticeable at the end of this time. The precipitate is washed with warm water,

[1] *Cf.* G. E. F. Lundell and H. B. Knowles, *Ind. Eng. Chem.*, 1920, **12**, 344; *J. Inst. Metals*, 1920, **24**, 475; G. E. F. Lundell, *J. Amer. Chem. Soc.*, 1921, **43**, 847.

[2] *Chem. Zeit.*, 1909, **33**, 1298. An account of analytical processes based upon the use of "cupferron" is given by S. A. Braley, *Ind. Eng. Chem.*, 1919, **11**, 1144.

[3] *Comptes rend.*, 1890, **111**, 914; *Chem. News*, 1881, **44**, 85; 1891, **63**, 10, 85, 172.

dissolved in hydrochloric acid, the solution evaporated to dryness, dissolved in hydrochloric acid, the silica filtered off, and the aluminium again precipitated as above, and weighed as $AlPO_4$, which contains 22·18 per cent. Al.

Copper, chromium, vanadium, and titanium, if present are precipitated together with the aluminium by this procedure. Copper is readily separated by means of hydrogen sulphide. Chromium in the precipitate may be determined by fusion with sodium carbonate and peroxide, acidifying the aqueous extract of the melt with sulphuric acid, and titrating with ferrous sulphate; or the aluminium phosphate may be reprecipitated by treating the acidified fusion extract with sodium phosphate and sodium acetate solutions. To remove vanadium the precipitate is dissolved in hydrochloric acid, a little sodium phosphate added, then sodium peroxide to convert the vanadium to pervanadic acid, and the aluminium phosphate reprecipitated by boiling with a slight excess of ammonia. Titanium may be separated by fusion with sodium carbonate and extraction with water, the titanium remaining insoluble, or it may be determined colorimetrically by means of hydrogen peroxide after dissolving the phosphate precipitate.

Modifications of this method have been described by Stead[1] and by Borsig.[2]

Zeigler[3] first eliminates silica, reduces the ferric chloride with sodium hypophosphite, precipitates the alumina with zinc oxide, repeats the precipitation after filtration and solution, again dissolves and precipitates twice successively with ammonia; after ignition a final purification is effected by fusion with alkali carbonates.

Schneider[4] has pointed out that all the above methods involve the use of reagents which may introduce more aluminium than is actually present in the metal. He therefore regards it as essential that the methods employed should involve the use of such reagents only as are easily obtained pure and easily tested, and from this standpoint has suggested the following method, in which the reagents are restricted to ammonia, tartaric acid, and ammonium sulphide.

Twelve grams of steel is dissolved in 150 c.c. of nitric acid of sp. gr. 1·2, and 12 g. of tartaric acid and 400 c.c. of ammonia (1 : 1) added. A bulky precipitate is formed, which redissolves to a very dark, clear solution on heating to 100°. The liquid is transferred to a two-litre flask, diluted with hot water, treated with 100 c.c. of ammonia (1 : 1) freshly saturated with sulphuretted hydrogen, the whole well shaken, allowed to cool, and made up to the mark. After the precipitate has settled, it is filtered through a dry filter paper, and 1500 c.c. of

[1] *J. Soc. Chem. Ind.*, 1889, **8**, 966. [2] *Stahl u. Eisen*, 1894, **14**, 6.
[3] *Dingl. polyt. J.*, 1890, **275**, 526; *J. Iron and Steel Inst.*, 1891, i., 440.
[4] *Oesterr. Zeitschrift*, **40**, 471.

the filtrate (=9 g. of metal) evaporated to dryness with nitric acid, and the residue gently ignited and treated with hydrofluoric and sulphuric acids to expel the silica. The residue thus obtained contains the oxides of vanadium and titanium, together with alumina; it is fused with alkali carbonate, the melt dissolved in sulphuric acid, and the alumina precipitated as usual.

The ether extraction process for the preliminary removal of the iron offers certain advantages for the determination of aluminium. From 5 to 10 g. of the sample is dissolved in hydrochloric acid and evaporated to dryness. The residue is lixiviated with dilute hydrochloric acid, the silica filtered off, the filtrate evaporated with addition of nitric acid to about 12 c.c., and extracted with ether. The aluminium is then precipitated as phosphate from the residual solution, as described on p. 82.

Tin.—Tin is quite an abnormal constituent of steel, but may be introduced by the use of tinplate scrap in the manufacture. It has sometimes to be determined in tinplate itself.

One method for the determination of the tin is to dissolve the tinplate in hydrochloric acid, filter, and treat the filtrate with sodium carbonate or ammonia until a slight precipitate is formed; this is redissolved and the liquid saturated with sulphuretted hydrogen. After standing, the precipitate is collected, warmed with potassium sulphide solution to separate tin sulphide from iron, lead, etc., and stannic sulphide precipitated from the filtrate by acetic acid; the precipitate is then evaporated in a porcelain crucible with nitric acid, ignited, and weighed as tin dioxide. One gram SnO_2 = 0·7881 g. Sn.

According to Mastbaum,[1] when tinplate is boiled for a few minutes with 8 to 10 per cent. hydrochloric acid, all the tin is dissolved, with very little of the iron. He digests not less than 25 g. of tinplate snippets from two to four times successively with 50 c.c. of 10 per cent. hydrochloric acid, boiling for five minutes in a beaker each time, and pours the solutions into a graduated 250 c.c. flask. From the appearance of the metal, it can easily be judged when all the tin has been dissolved. After making up to the mark, 50 c.c. of the solution is withdrawn with a pipette, ammonia added to incipient precipitation, and then 10 c.c. of yellow ammonium sulphide; the liquid is then well shaken and made up to 100 c.c. Fifty c.c. of the clear tin sulphide solution (= 2·5 g. of tinplate) is diluted, acidified with acetic acid, the precipitate allowed to settle, rinsed on to a filter with 10 per cent. ammonium acetate solution, the precipitate dried and ignited to oxide, with repeated moistening with ammonium carbonate. If preferred, the sulphide solution may be taken directly to dryness and ignited.

[1] *Z. angew. Chem.*, 1897, 10, 330.

The chlorine method of Lunge and Marmier[1] is considerably more rapid. Two to three grams of tinplate is cut into strips, introduced into a bulb-tube, and heated in a current of dry chlorine at a low temperature so that the tin tetrachloride distils off, while the ferric chloride, if formed at all, does not volatilise. The further end of the bulb-tube is prolonged into the limb of a Peligot's U-tube charged with water, to which a second U-tube and a small conical flask are attached. Tin tetrachloride begins to distil off in the cold; as the reaction slackens, heat is gently applied, and after two to three hours the surface of the iron appears uniformly brown without white specks. Any tin chloride remaining in the U-tube is driven over by the aid of a small flame, and the chlorine is then displaced by a current of carbon dioxide. The end of the bulb-tube is cautiously washed out with dilute hydrochloric acid, taking care to avoid dissolving the ferric chloride; the receivers are similarly treated and the united liquids neutralised with ammonia until a slight precipitate is produced, which is redissolved by a drop or two of hydrochloric acid. The tin is then precipitated, either as metastannic acid by means of ammonium nitrate, or as sulphide.

Tin may be determined volumetrically by dissolving the tinplate in hydrochloric acid in a flask through which a stream of carbon dioxide is passed to prevent oxidation of the solution, cooling, and titrating with iodine solution using starch as indicator. (See Tin, p. 260.)

Zirconium. — It may occasionally be necessary to determine zirconium in steel or to establish its absence. According to Ibbotson, the most satisfactory method is to precipitate the basic chloride by boiling with a large excess of sulphurous acid. Sulphates and nitrates must be absent and hence to prepare the solution 5 g. or more of the steel is dissolved in hydrochloric acid, the residue is filtered off, ignited, fused with potassium hydrogen sulphate and the melt dissolved in water, precipitated with ammonia, filtered, and the precipitate washed, dissolved in hydrochloric acid and added to the original solution. The whole of the solution is now evaporated to a pasty condition, diluted with 250 c.c. of boiling water (there should be just sufficient acid remaining to prevent the formation of any turbidity at this stage), 25 c.c. of saturated sulphur dioxide solution added, and the solution boiled for about ten minutes. Any precipitate formed is filtered off, washed with hot water containing sulphurous acid and ignited to ZrO_2. If the precipitate is seriously contaminated with iron, the operations should be repeated. Any titanium in the sample will be obtained with the zirconium, and it may be determined colorimetrically by fusing the ignited precipitate with potassium hydrogen sulphate and treating the fusion extract with hydrogen peroxide; or the zirconium may be

[1] *Z. angew. Chem.*, 1895, 8, 429.

separated as phosphate from the solution in the presence of excess of hydrogen peroxide. For this precipitation, the solution should contain about 1 per cent. of free sulphuric acid, and should be allowed to stand for some hours after adding the sodium phosphate. Sufficient hydrogen peroxide must be present to keep the titanium in solution as yellow pertitanic acid. The ignited zirconium phosphate contains 51·8 per cent. ZrO_2.

Uranium.—This element has been used to some extent as a substitute for tungsten in tool steels. It may be precipitated as phosphate from a solution containing iron in the ferrous condition. For its determination, 5 to 10 g. of the steel is dissolved in hydrochloric acid and the solution diluted and filtered, if necessary. Any residue is ignited, again treated with acid and the solution added to the main filtrate. An excess of microcosmic salt is now added to the hot solution, followed by dilute ammonia, until a slight permanent precipitate is produced. The solution is cleared with a few drops of acid and then 10 g. sodium thiosulphate and 20 c.c. acid are added and the whole boiled for about ten minutes. The precipitate is filtered quickly and washed with water containing a little acetic acid and ammonium acetate.

Iron and chromium may be eliminated from the uranyl phosphate precipitate by dissolving in hydrochloric acid, adding sodium peroxide until strongly alkaline, then several grams each of sodium and ammonium carbonates. The ferric hydroxide formed is filtered off and the uranium is reprecipitated as above. Chromium remains in solution as chromic acid.

If aluminium is present, it accompanies the uranium throughout and is weighed as orthophosphate. An approximate separation may be effected by dissolving the mixed phosphates in nitric acid, nearly neutralising with ammonia, and pouring the solution into a large excess of ammonium carbonate solution (Brearley).

If the amount is small, a direct determination of the uranium in the precipitate may be made colorimetrically by comparing the colour obtained on adding a mixture of potassium carbonate and sodium peroxide to its solution with that produced with a standard uranium solution. Larger quantities may be titrated with permanganate solution after reduction with zinc.

Boron. — Boron may be determined in special boron steels as follows[1]:—One to three g. of the steel is dissolved in dilute sulphuric acid in a flask fitted with a reflux condenser, care being taken to avoid too large an excess of acid. The solution is transferred to a distillation flask connected with an inverted condenser, the end of which passes through a cork in a receiver containing a 2 per cent. solution of sodium

[1] C. Aschman, jun., *Chem. Zeit.*, 1916, **40**, 960 ; *J. Soc. Chem. Ind.*, 1917, **35**, 1263.

hydroxide. The outlet tube from the receiver dips into a beaker of water. The distillation flask is heated on a sand bath until nearly the whole of the liquid has distilled over. The apparatus is allowed to cool a little, 10 c.c. of absolute methyl alcohol (free from acetone) introduced, and the liquid distilled. This operation is repeated five times, a slow current of air passed through the apparatus for some minutes after each addition of methyl alcohol and for fifteen minutes after the final distillation. The distillate is heated to expel alcohol, then boiled, and neutralised to methyl orange with hydrochloric acid. Glycerol or mannitol is added and a few drops of phenolphthalein, and the solution titrated with standard sodium hydroxide to a violet coloration.[1]

Cerium.—The commercial pyrophoric alloys, which are composed of iron and cerium, may be analysed by the method recommended by H. Arnold.[2] From half to one gram of the sample is dissolved in hydrochloric acid containing bromine. After the addition of 0·5 g. potassium chlorate the solution is evaporated to dryness to render the silica insoluble and is then taken up with acid and filtered. To the filtrate, 3 to 5 g. tartaric acid is added and the solution is poured into 50 c.c. strong ammonia. The solution is heated to 60°, 15 to 30 c.c. ammonium sulphide added and the liquid well stirred. The precipitate, which contains all the iron with any copper or zinc which may be present, is filtered off, washed with water containing ammonium sulphide and tartrate, ignited to oxide, and separately examined for copper and zinc.

The cerium is determined in the filtrate by evaporation, followed by two evaporations with nitric acid and potassium chlorate to remove the tartaric acid. The residue is dissolved in dilute acid and the cerium precipitated as oxalate. If aluminium is present it will be found in the filtrate.

A method for the precipitation of cerium as peroxyacetate is described by K. Swoboda and R. Horny.[3]

Oxygen.—The accurate determination of oxygen has received much attention. The process on which the later methods have been based is that due to Ledebur,[4] in which the oxides are reduced by means of hydrogen and the resulting water collected and weighed. Iron containing enclosed slag gives meaningless results by this method, since a part, at any rate, of the silicate oxygen is determined together with the oxide oxygen.

To carry out the determination, 15 g. of fine borings are placed

[1] Raulin, *J. Soc. Chem. Ind.*, 1912, **30**, 899.
[2] *Z. anal. Chem.*, 1914, **53**, 496.
[3] *Z. anal. Chem.*, 1926, **67**, 386; *J. Soc. Chem. Ind.*, 1926, **45**, B 242.
[4] *Stahl u. Eisen*, 1882, **2**, 193.

in a previously ignited porcelain boat and introduced into a combustion tube, drawn out at the end and connected to a U-tube charged with phosphoric oxide; this is protected by a guard-tube containing strong sulphuric acid. A Kipp's hydrogen generator, a wash-bottle charged with alkaline lead solution, a small tube with platinised asbestos kept at dull red heat (to remove oxygen), a U-tube containing sulphuric acid and another containing phosphoric oxide are placed in front of the combustion tube. Hydrogen is passed through the apparatus for an hour or two; the combustion tube is then heated, and the boat kept at a bright red heat in a current of hydrogen. After allowing to cool, the current of hydrogen is displaced by air, and the absorption

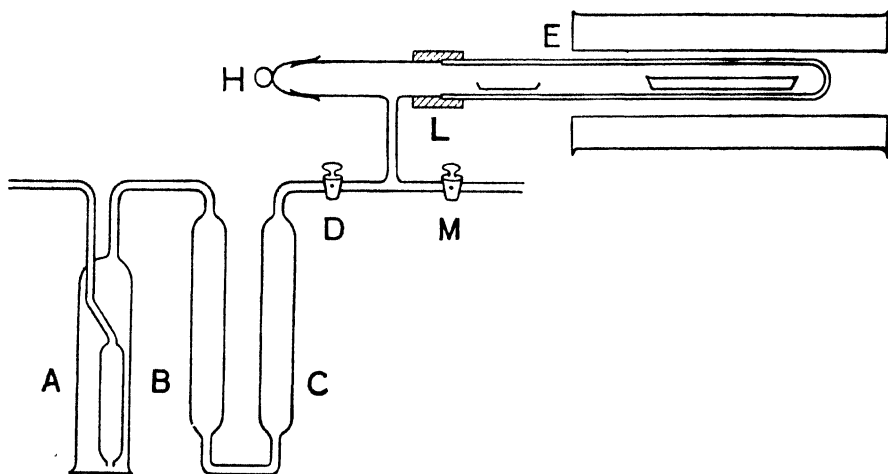



Fig. 13.

tube detached and weighed. The loss in weight of the boat serves as a check upon the oxygen absorbed as water. Owing to volatilisation of the sulphur and carbon the former is, however, invariably greater than the latter; if the contrary should be the case, extraneous oxygen must have passed into the combustion tube. In a modification of this process the steel is first heated in a stream of pure dry nitrogen before being heated in hydrogen, but this is unnecessary.

A method devised by J. A. Pickard[1] also consists in heating the sample in dry hydrogen and weighing the water formed. It is carried out in a special vitreous silica tube E, 18 inches by 1 inch in internal diameter, shown in Fig. 13. This tube is connected by a gas-tight rubber joint with the glass extension of the same diameter which carries a side tube L and is closed by a glass cap H, which fits over

[1] *Iron and Steel Inst.: Carnegie Scholarship Memoirs*, 1913, 5, 70.

the end. The side tube L carries two stopcocks D and M on a T-piece. D is connected with the hydrogen supply and M with a Fleuss pump. The silica tube is held horizontally in a strong clamp, in such a manner that an electric furnace can be placed round it for 9 or 10 inches of its length, and can be removed at will without disturbing any part of the apparatus. The water resulting from the reduction is absorbed by phosphoric oxide contained in a small glass boat inserted into the open end of the tube near the glass cap.

Before carrying out a determination, the nickel boat used for the sample is inserted into the tube, and a boat of phosphoric oxide placed in the cold end of the tube; a stream of hydrogen bubbled through A containing sulphuric acid and B containing solid caustic potash is passed through and the tube heated up. After allowing to cool, the nickel boat is removed, weighed, and 20 g. of the steel drillings or turnings placed in the boat. The small glass boat containing phosphoric oxide is weighed in a special weighing bottle. The boat containing the drillings is now placed in the silica tube near the closed end and a small unweighed boat containing phosphoric acid placed near the open end. The cap is replaced and the tube evacuated and allowed to remain so for a minute or two, during which time any moisture or air condensed on the drillings are completely removed. Hydrogen is now admitted up to atmospheric pressure and the weighed boat of phosphoric oxide is substituted for the unweighed boat. While this change is being made the hydrogen completely escapes from the tube and is replaced by the same volume of laboratory air. A correction is made for the amount of water vapour thus introduced, but this never amounts to more than 1 or 2 mgms. The tube is now exhausted. filled with hydrogen and re-exhausted, these operations being repeated. Hydrogen is now admitted up to half or two-thirds atmospheric pressure, which is easily arranged by making the volume of the purifying apparatus between tap D and the tap on the hydrogen Kipp from one to two times that of the silica tube. Then by shutting off the Kipp and making connection through D with the evacuated tube, the latter is filled with hydrogen at a diminished pressure, which is necessary in order to prevent the cap being blown off by the increased pressure due to the expansion of the gas on heating. The electric furnace, previously heated to 1000°, is now pushed over the end of the tube until 9 or 10 inches are surrounded; it is allowed to remain there for three-quarters of an hour, after which time the furnace is removed and the tube allowed to cool. When cold it is filled with hydrogen at atmospheric pressure, tap D closed, the cap removed and the phosphoric oxide boat quickly replaced in the weighing bottle and weighed. The loss in weight of the steel is always slightly greater than the gain in weight of the phosphoric oxide, owing to loss of sulphur and carbon.

The complete apparatus required for this method is supplied by Messrs John Orme & Co., 148 High Holborn, London.

Pickard's method has been modified in several directions by T. E. Rooney,[1] who uses calcium chloride as a drying agent instead of phosphoric oxide, and a specially arranged electric furnace consisting of an alundum tube wound with platinum ribbon and capable of giving a temperature of 1300°. The best temperature for complete reduction was found to be between 1150° and 1200°, which confirms the results obtained by J. H. Whiteley[2]; the time required is about two hours.

P. Oberhoffer and O. von Keil[3] have modified the method by mixing the drillings with an alloy of tin and antimony previous to treatment in hydrogen, in which case the temperature necessary does not exceed 1000°, so that an ordinary nichrome wound furnace may be used.

Nitrogen.—Nitrogen occurs in samples of iron and steel, especially after electric arc welding, chiefly as the nitride Fe_2N, and is determined by solution of the sample in dilute acid, whereby the nitrogen is obtained as an ammonium salt. This is then distilled with caustic alkali or lime and the ammonia evolved collected in dilute sulphuric acid and determined by Nessler's reagent, or by titration of the iodine liberated from potassium iodide-iodate solution with thiosulphate solution. The latter method appears to give the most reliable results.

Pure ammonia-free water is required for the determination, and for this purpose 10 per cent. of an alkaline potassium permanganate solution is added to the water which is distilled until the distillate shows freedom from ammonia with Nessler's reagent, then ordinary distillation is carried on. It is advisable to use a condenser tube of tin. The alkaline permanganate solution is made by dissolving 200 g. potassium hydroxide and 8 g. potassium permanganate in 1100 c.c. water and concentrating by boiling to 1000 c.c.

Colorimetric Method.[4] One gram of the sample is dissolved in 20 c.c. redistilled hydrochloric acid of sp. gr. 1·124; the solution is filtered, added to 20 c.c. potassium hydroxide solution, which is equivalent to 20 c.c. hydrochloric acid sp. gr. 1·124, in a suitable distillation flask. The solution is distilled and to the distillate 2 c.c. standard Nessler's reagent, diluted to 10 c.c., is added and the solution made up to 150 c.c. The colour of the solution is now matched to the colour obtained with a standard solution made by dissolving 0·038147 g. ammonium chloride in 1 litre of water (1 c.c. = 0·01 mg. N). Three c.c.

[1] *J. Iron and Steel Inst.*, 1924, ii., 122.

[2] *Ibid.*, 1920, ii., 143.

[3] *Stahl u. Eisen*, 1921, 41, 1449; *J. Iron and Steel Inst.*, 1922, i., 651.

[4] *Cf.* H. Braune, *Jernkontorets Ann.*, 1906, 59, 671.

of this solution is used for comparison by treating with Nessler's reagent and diluting to the same colour intensity as the distillate. The nitrogen content is calculated from the relative volumes.

Volumetric Method.[1] Five grams of the steel is placed in a round bottomed flask of about 250 c.c. capacity fitted with a dropping funnel, condenser, and bubble U-tube by means of glass connections and ground glass joint (Fig. 14). About 10 c.c. hydrochloric acid sp. gr. 1·12 is placed in the bubble tube to seal the gas passage. Forty c.c. hydrochloric acid (sp. gr. 1·12) is introduced through the dropping funnel and the flask is gently warmed. The steel dissolves rapidly and the evolved gases pass through the water-cooled condenser and out through the

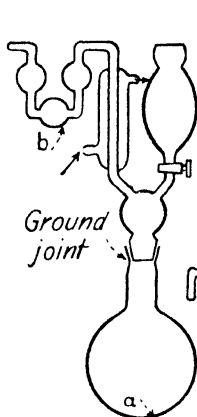
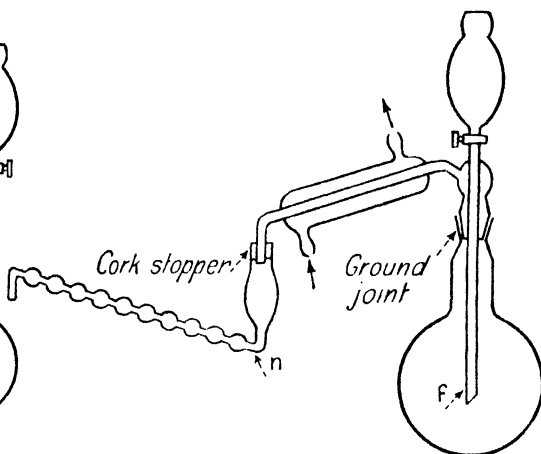
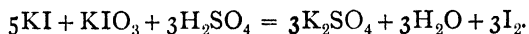



Fig. 14.—Dissolving Flask. Fig. 15.—Distilling Flask.

bubble tube. Any vapours are condensed and returned to the flask from the condenser and any ammonia evolved is retained by the acid in the bubble tube. When the steel is completely dissolved, all the nitride nitrogen remains as ammonium chloride in the flask, with the exception of traces of ammonium chloride in the bubble tube. The contents of this tube and the flask are washed into the dropping funnel of the distilling flask. This flask (Fig. 15) has a capacity of about 1 litre and is connected to a dropping funnel and condenser by a ground glass joint. The condenser is afterwards connected with a suitable receiver, *n*, containing *N*/100 sulphuric acid for the collection of the evolved ammonia. Fifty c.c. of sodium hydroxide solution, free from nitrites and equivalent to the hydrochloric acid used for making the solution, 300 c.c. water and 10 c.c. alkaline permanganate solution (8 g. $KMnO_4$, 200 g. NaOH dissolved in 1 litre water), are placed in the distillation flask together with small coils of nichrome wire to ensure quiet boiling.

[1] F. Hurum and H. Fay, *Chem. and Met. Eng.*, 1922, **26**, 218.

This liquid is boiled until a part of it is distilled over. The receiver mentioned above, containing 10 c.c. or a larger exactly measured amount of *N*/100 sulphuric acid, is now attached to the condenser, and the ferrous sulphate solution contained in the dropping funnel is gradually run down into the distilling flask. The boiling immediately accelerates as the liquid in the distilling flask gives off ammonia and hydrocarbon gases, and the ammonia, together with water vapour given off, begins to collect in the water-cooled condenser and runs down into the receiver. After a few minutes' boiling, all the ammonia will have passed over and combined with the sulphuric acid. Violent boiling and detrimental shocks are apt to occur when distillation has proceeded for a certain time, and for this reason it is advisable to retain a small part of the ferrous solution in the dropping funnel instead of adding all of it to the distilling flask at the beginning. When the last drops of the ferrous solution are added to the distilling flask, the further evolution of gas revives the boiling of the alkaline liquid and prevents accidents. Distillation is continued until about 50 c.c. has been collected in the receiver, and the distillate, containing all the ammonia as ammonium sulphate is poured into a beaker. Four c.c. of a 5 per cent. solution of potassium iodide and 2 c.c. of a 5 per cent. solution of potassium iodate in water are added, and the liberated iodine is titrated with *N*/100 sodium thiosulphate, made by dissolving 2·5 g. of crystallised sodium thiosulphate in pure water and diluting to 1 litre. The sulphuric acid as used in the receiver, is valued by taking 10 c.c. or exactly the amount used in the receiver, the same amounts of iodide and iodate are added, the liberated iodine titrated with sodium thiosulphate solution. The difference between the two values obtained represents the amount of sulphuric acid equivalent to the ammonia absorbed, according to the equation:—

$$5KI + KIO_3 + 3H_2SO_4 = 3K_2SO_4 + 3H_2O + 3I_2.$$

The above method is a modification of that used by J. H. Paterson and H. Blair,[1] and differs in the determination of the excess acid iodometrically. This obviates the necessity of using methyl orange or methyl red as indicator, both of these being distinctly unsatisfactory with dilute solutions such as are employed.

Slag.—No trustworthy method is known for determining the enclosed slag in iron or steel; the following fairly satisfactory method has been worked out by Eggertz. From 2 to 5 g. of the sample is placed in a beaker with five times the weight of iodine, and the same amount of water, the whole cooled in ice, and stirred until the iron has dissolved. The liquid is then diluted, allowed to settle, and decanted through a filter; the residue is treated with very dilute hydrochloric acid, filtered,

[1] *J. Soc. Chem. Ind.*, 1919, 38, 328.

thoroughly washed, ignited, and weighed. The carbon is thus burnt off and the slag left behind. If the iron contains much combined silicon there will be an admixture of silica in the residue, which is removed by digesting it in a platinum vessel, before igniting, first with concentrated and then with dilute sodium carbonate solution.[1]

Combustion of the sample in chlorine, free from hydrochloric acid and oxygen, may be used for the volatilisation of iron, etc., as chlorides; the residue is then examined for slag.

LITERATURE.

BERINGER, C. and J. J.—*A Text-book of Assaying*, 1921.
BLAIR, A. A.—*The Chemical Analysis of Iron*, 7th edition, 1908.
BREARLEY, H., and IBBOTSON, F.—*The Analysis of Steelworks Materials*, 1902.
CAMPION, A.—*Iron and Steel Analysis*, 1910.
COMMITTEE OF THE CHEMICAL SECTION OF THE ENGINEERS' SOCIETY OF WESTERN PENNSYLVANIA.—*Methods of Iron Analysis*, 1898.
FRESENIUS, R.—*Quantitative Chemical Analysis*, 7th edition, vol. ii. translated by C. E. Groves, 1900.
IBBOTSON, F.—*The Chemical Analysis of Steel Works' Materials*, 1920.
JOHNSON, C. M.—*Rapid Methods for the Chemical Analysis of Special Steels, Steel-making Alloys and Graphite*, 1909.
MOORE, R. B.—*Analytical Methods for Certain Metals*, Bulletin 212, Department of the Interior, Washington Government Printing Office, 1923.
SCHOELLER, W. R., and POWELL, A. R.—*The Analysis of Minerals and Ores of the Rarer Metals*, 1919.
SCOTT, W. W.—*Standard Methods of Chemical Analysis*, 4th edition, 1925.
SUTTON, F.—*Volumetric Analysis*, 11th edition, 1924.
TREADWELL, F. P., and HALL, W. T.—*Analytical Chemistry: Quantitative Analysis*, 5th edition, 1919.

---

[1] Cf. *Stahl u. Eisen*, 1912, **32**, 1664.

NON-FERROUS METALS

By C. O. BANNISTER, M. Eng., A.R.S.M., F.I.C., Professor of Metallurgy, University of Liverpool; and GEORGE PATCHIN, A.R.S.M., M.I.M.M., Principal and Head of the Metallurgy Department, the Sir John Cass Technical Institute, London.

THE dry metallurgical assays described in this section are restricted to those used for silver, gold, lead, and tin. The dry methods for silver and gold are as rapid and as accurate as the ordinary methods of analysis.

The chemical examination of ores, works' products, and metals is usually preceded by some mechanical treatment, in order to obtain a true average sample, and to prepare the sample for the assay.

PREPARATION OF THE SAMPLE

In addition to the various types of grinding apparatus described in Vol. I., pp. 12 *et seq.*, the following may be mentioned:—

Fig. 16, a cast iron mortar and an iron pestle with a wooden handle about 4 feet long.

Fig. 17, a bucking plate with heavy bucking hammer.

Fig. 18, combined mortar and pulveriser.

For the fine grinding of hard ore samples, a set of small cast iron rolls or a disc grinder is often used, the ground material being received in a wooden or metal receptacle.

Malleable particles, such as metals, silver glance, hornsilver, left behind on sieving pulverised ores, slags, sweeps, etc., must be kept separate, and their weight and proportion to the total weight of the sample noted. These may either be assayed separately, or a proportional amount may be added to the sieved sample taken for analysis (*cf.* Assay of Sweep, p. 132).

Estimation of Moisture. The moisture in powdered ore samples must first be determined as they come from the concentrating floors. Up to 1 kg. of the powdered ore is weighed into one of a series of sheet iron trays and kept at a temperature not much over 100°, the contents being

stirred with an iron spatula, until a glass plate, placed on the sample for about a minute, no longer shows a deposition of moisture, and two successive weighings agree. The dried samples are then transferred

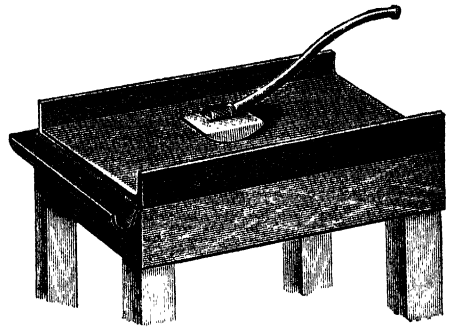
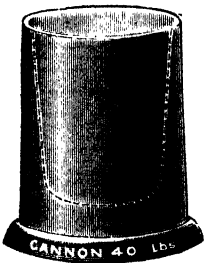



Fig. 17.

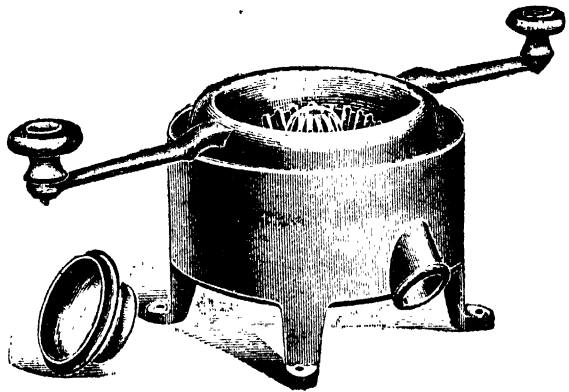



Fig. 18.

either to bottles, sheet iron boxes, or to paper packets.

In some English works exactly 1 lb. of the sample, powdered to pass through a sieve of $\frac{1}{16}$ inch mesh, is gently heated in an iron tray or pan. When a cold glass plate or polished brass weight indicates that there is no further evolution of moisture, the whole is weighed and the result expressed in grains per seven thousand.

Fig. 16.

All samples should be retained for several months, or, at any rate, until all questions relating to sale or purchase have been settled. If the powdered samples are sent by post or rail, so that they are shaken

in transit, the constituents may become separated owing to their different specific gravities. The whole sample should then be turned out on to a sheet of paper and thoroughly re-mixed before weighing out the portion for analysis; if this is not done, serious errors may result.

THE SAMPLING OF METALS AND OF ALLOYS

The sampling of metals and of alloys may be effected by the dipping and granulation method.

Portions of the ingots or plates, or whole ingots of the noble metals, are melted in a graphite crucible in a wind-furnace, the metal being covered with charcoal; the whole is stirred with an iron rod, or better, with a piece of fire-clay (Salamander rod), and a sample is taken by dipping with an iron spoon, coated with fire-clay, or by means of a charcoal rod, in which a suitable hole has been cut. This sample is then poured in a thin stream into an iron bucket containing water, the water being agitated by means of a bundle of twigs. When the small portion is removed by the charcoal sampler, the usual practice consists of flattening out the metal after it has solidified.

This method is unsuitable for zinc alloys on account of the unavoidable loss of zinc through volatilisation.

The ingot method of sampling is more convenient and more frequently employed than the granulation method. In taking the sample, however, it is necessary to realise the possibility of segregation having taken place during the solidification of the metal, and to select that part of the ingot which would show an average amount of segregation. Samples are taken from filed or chisel-dressed portions of ingots or plates by means of drills or a hollow punch (Fig. 19), the pieces being taken from the upper and under surfaces, and from opposite upper and lower edges or corners and mixed together, or approximately equal quantities of each may be weighed. In ascertaining the fineness of ingots of noble metals, the samples from various parts are assayed separately and the mean result taken or the samples are melted together for subsequent granulation.

FIG. 19. (½ actual size.)

Punch samples are flattened out on a polished anvil, with a polished steel hammer, or by means of a small rolling mill (Fig. 20), but drillings should be sufficiently fine to require no further treatment.

Bronzes rich in tin, samples of bearing metals, etc., which need to be reduced to drillings, etc., for analysis, are often handed to the analyst in the form of small compact pieces, which cannot be sampled, either by filing or by drilling. Small pieces may then be cut off with a cold chisel, the material being placed for the purpose on a bronze or copper plate. The chips may be flattened, as far as possible, with a hammer.

Ingots, blocks, or large pieces of alloys that are not homogeneous (tin, lead and antimony alloys, and white metals) should be drilled through at a point about one third of the distance from the two edges

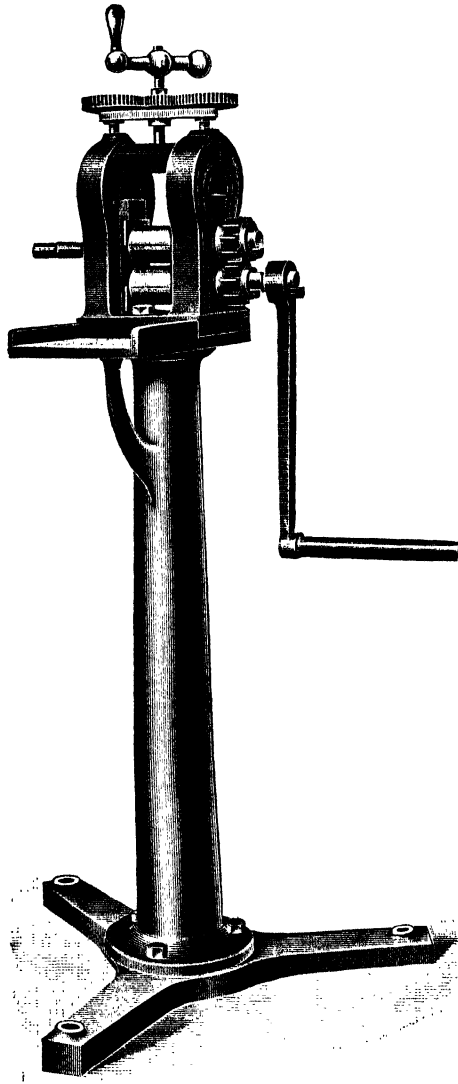



Fig. 20.

of the top, with a small drill, the fine borings being thoroughly mixed. If the amount of drillings is considerable, say, from a number of ingots, a small ingot is produced by melting the drillings together under palm oil and casting in an iron mould, which is then sampled by drilling,

or the molten mass may be poured on to a cold, clean, iron plate, and samples subsequently cut from different parts with a pair of shears.

In lead-antimony alloys, according to H. Nissenson and P. Siedler,[1] a diagonal saw-cut through a block of the alloy gives the most satisfactory sample. The sample is well mixed, reduced, and sieved, the larger particles, rich in lead, and the fine particles, rich in antimony, are separately analysed and the results adjusted. In a block of hard lead, the antimony in the upper portion was found to be 21·64 per cent., in the middle 19·98 per cent., and in the lower portion 12·08 per cent.; by the method of sampling and analysis described, the mean result obtained was 18·31 per cent.

In sampling argentiferous lead, the procedure depends on the amount of silver present. For pigs or bars containing up to 20 oz. of silver per ton, chips are cut from the top and bottom of a proportion of the consignment or of every bar with a chisel, all the chips are melted together, and a small bar is cast, from which the sample is taken. Pigs containing between 20 and 200 oz. of silver per ton are best sampled by means of a circular saw, the sawings from a diagonal cut across the pigs being collected, melted down, and cast as above. When the lead contains over 200 oz. of silver to the ton, or whenever 1 oz. of gold is present, it is necessary to melt down the whole consignment and to take a dip sample.

Samples of zinc slabs are generally taken by means of a circular saw, and the volume of a definite weight of sawings is a useful indication of the purity of the metal; impure metal gives short brittle sawdust, and pure metal a long shaggy product.

All brittle alloys and materials may be crushed and sieved for sampling, exactly like ores.

Impurities in Samples.

Particles of iron are removed by spreading the sample on paper and passing a strong horse-shoe magnet through it.

If the drillings are made by a mechanic, it is necessary to see that neither oil nor any soapy material is used for lubricating purposes; the drillings should be received on a sheet of paper.

Samples delivered to the laboratory in the form of drillings must always be looked upon with suspicion. In iron and steel the presence of pieces of other metals can be detected by the colour; these must either be picked out or evenly distributed. The presence of oil, etc. can be detected by the vapour evolved, or by the odour produced, on heating in a test tube; in addition, dirt, sand, wood splinters, and paper are often present. The drillings can be cleaned by treating them in a beaker with chloroform, ether, or benzene, which is allowed

[1] *Berg u. Hütten. Zeit.*, 1903, 64, 421; *J. Soc. Chem. Ind.*, 1903, 22, 1246.

to remain in contact with them for ten minutes, and then well stirred for one or two minutes, the coloured and dirty liquid poured off, and the drillings again treated with fresh solvent; finally, they are washed twice with absolute alcohol and dried rapidly in a shallow porcelain dish on the water-bath. After removing any iron from non-ferrous samples by means of a magnet, the fine material and sand are sieved out.

Filings should only be made with a perfectly clean or new file. Some metals and alloys rapidly foul the file and may be more conveniently sampled by means of a hack saw.

WEIGHING

For weighing out ores, etc., for analysis, any sufficiently delicate balance may be used. In assay laboratories, a simple quick-arrest ore balance (Figs. 21 and 22), provided with removable nickel pans, and

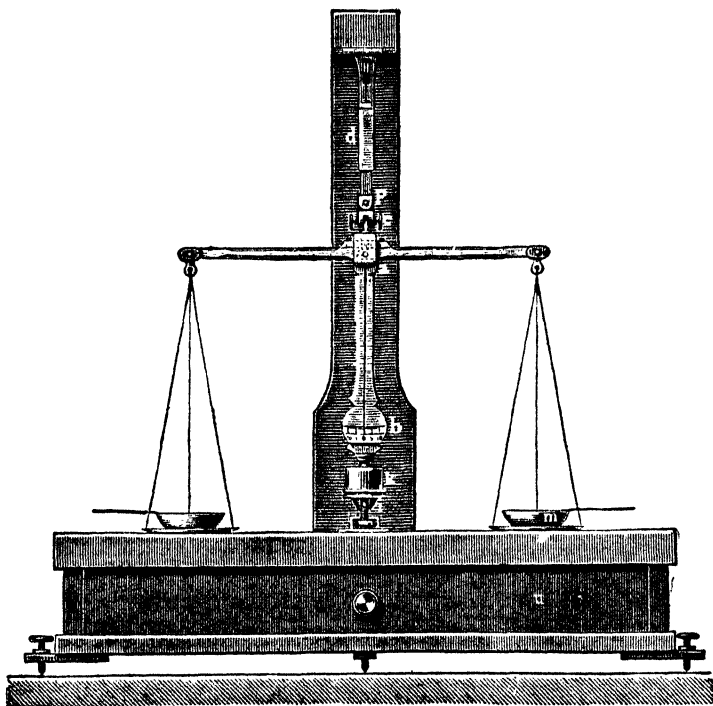
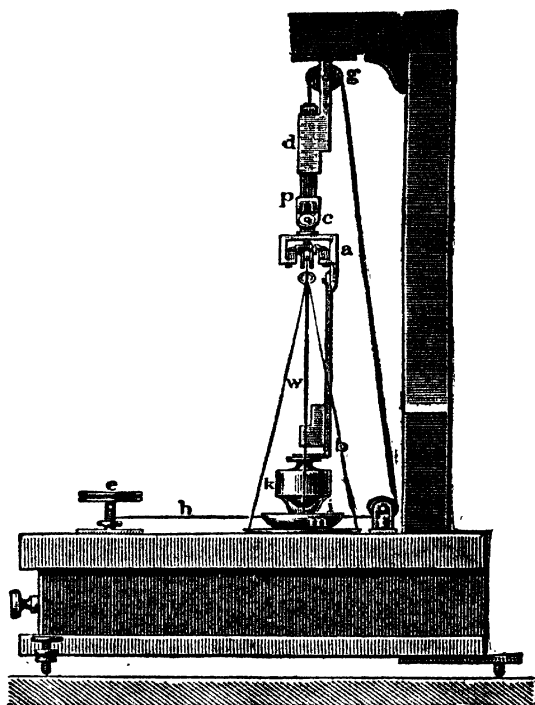
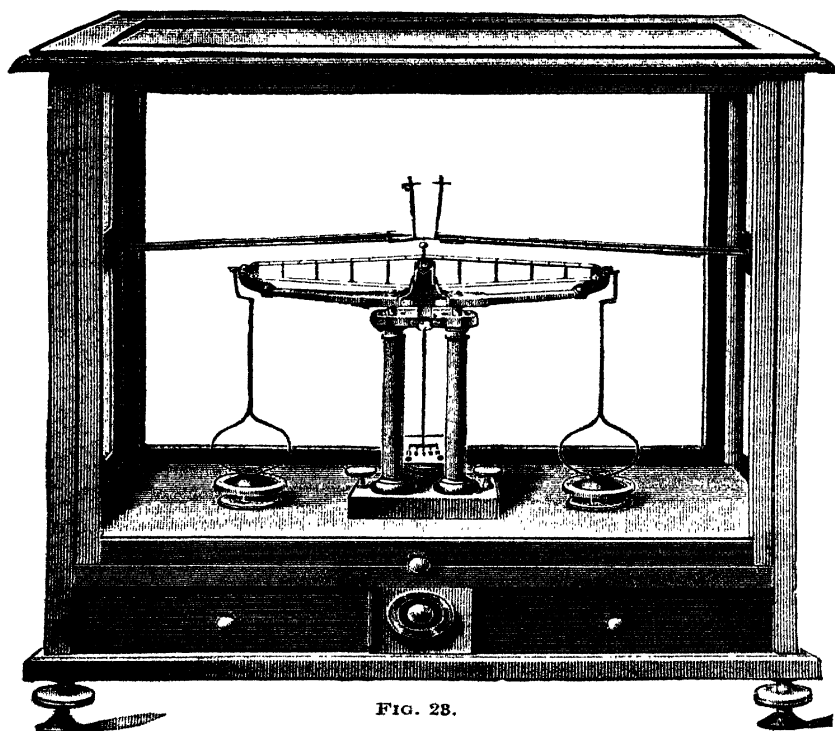



FIG. 21.

sensitive to 1 mg., with a load of 50 g., is used. A horn or metal scoop with a corresponding balance weight is convenient for transferring the weighed sample to the vessel in which it will be treated and obviates the use of removable balance pans or counterpoised watch glasses.

For weighing noble metals and their alloys, assay balances (Fig. 23) are employed, which are sensitive to 0·05 to 0·01 mg., with a load of 2 g.

FIG. 22.

FIG. 23.

SILVER

The materials which have to be assayed for their value in silver include the following:—Silver-bearing ores, metallurgical products (such as furnace lead, products of the desilverisation of lead, skimmings, litharge, test-hearth material, lead and copper mattes, speiss, scoriæ, flue-dust, slags, blister copper, crude silver, refined silver), silver-bearing solutions, cement silver, silver sulphide, amalgams, and residues from amalgamation and other extraction processes, silver alloys and sweeps from their manufacture, silver-plated goods, plating liquors, etc.

The dry method of assay is to be recommended for most of these; the wet method is employed for silver itself (crude and refined silver, bar silver), silver alloys, such as bullion, etc., solutions and silver baths, the strength of which can be accurately determined by precipitation or by titration. Occasionally the wet and dry methods are combined.

Silver Ores.

The most important silver minerals occurring in ores are:—

Mineral.	Per Cent. Silver.
Native Silver, with not infrequently small quantities of gold, mercury, copper, iron, arsenic, and antimony	...
Antimonial silver or *dyscrasite*	up to 94
Argentite or *silver glance*, Ag_2S	87·1
Polybasite, $9(CuAg)_2S$, $(SbAs)_2S_3$	72
Stephanite, $5Ag_2S$, Sb_2S_3	68
Pyrargyrite, $3Ag_2S$, Sb_2S_3	59·8
Miargyrite, Ag_2S, Sb_2S_3	37·2
Proustite, $3Ag_2S$, As_2S_3	65·5
Stromeyerite, or silver copper glance, Cu_2S, Ag_2S	53
Freieslebenite, $5(PbAg_2)S$, $2Sb_2S_3$	23
Silver amalgams	up to 95
Kerargyrite, or *horn silver*, AgCl	72·5
Bromite, AgBr	57·4
Embolite, which includes isomorphous mixtures of chloride and bromide of silver, varying in composition from AgCl + 3AgBr to AgBr + 3AgCl	up to 70
Iodite, AgI	46
Hessite, Ag_2Te	61
Tetrahedrite, or *fahl ore*, which is a mixture of antimony or arsenic sulphide, or both, with sulphides of silver, copper, zinc, iron, or mercury, and which may contain from a fraction of 1 per cent. up to 31 per cent. of silver. When antimony and arsenic are both present, the silver seldom amounts to 1 per cent.	...

A considerable proportion of the silver produced is obtained from argentiferous galena and other lead and copper ores, and not from silver ores proper.

Dry Methods of Silver Assay

The dry methods of silver assay consist in dissolving out the silver (and gold) by means of pure lead by fusion, the lead button obtained being subsequently cupelled. Two methods are in use for producing the lead button, viz., scorification and the pot or crucible methods.

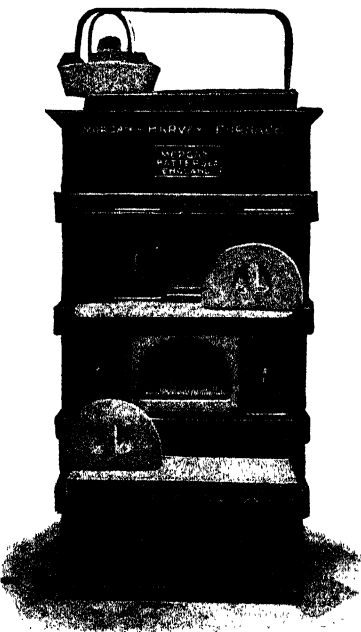
I.—Dry Assay for Ores, etc. (excluding silver alloys)

1. The Extraction with Lead.

(a) Scorification.—The process is carried out in a muffle furnace, heated with coal, coke or gas (or with benzine, petroleum, etc.), and connected with a chimney. In many assay offices gas muffles are exclusively employed for scorifications and cupellations; the advantages are cleanliness and exact regulation of temperature, with consequently smaller silver losses in the assay. A portable form of muffle furnace for coal or coke is shown in Fig. 24.

Fig. 24.

Manipulation. Usually from 4 to 5 g. of the finely powdered sample is weighed out on a balance such as that shown in Fig. 21, p. 99; a smaller quantity of materials rich in silver may be taken, and from three to five times as much of very poor material, but correspondingly large scorifiers must then be used.

One half of the necessary quantity of finely granulated assay lead is well mixed with the powder in a scorifier, the remainder is evenly spread on the top and finally, if necessary, a little borax is added. If much silica is present in the ore, slagging will be facilitated by an addition of litharge, free from silver or of known silver content.

When less than 30 oz. of silver per ton is present it is usual to weigh out three lots and to carry out three scorifications; with a content of more than 30 oz. per ton, six scorifications should be

made, the actual result being taken from the mean weight of all the silver beads, weighed separately. If the approximate silver content of the material to be assayed is not known, a preliminary test is made. This method of working is founded on the fact that the distribution of silver in rich ores is not uniform.

The quantity of assay lead required depends on the character of the material. Pure lead ores require only six times their weight of lead; the same holds good for hard-lead.

Materials containing fair amounts of iron and zinc require considerably more lead, from ten to fifteen times the weight of the ore taken; those containing much copper, nickel, or tin require up to thirty times their weight. Similarly, the quantity of borax needed varies; as this must be anhydrous it is advisable to use powdered borax glass. It is used to increase the fluidity of the slags in materials containing much gangue and metallic oxides difficultly soluble in lead oxide, and it should be added in small quantities from time to time, as required.

The following table will be a useful guide to the amount of lead and fluxes necessary with different classes of ores and materials :—

Material.	Amount taken.	Lead.	Flux (Borax Glass).
	g.	g.	g.
Siliceous ores	5	60	0·5
Ferruginous ores	5	50	2·0
Pyritic ores	5	70	1·0
Cupreous ores	5	80	1·0
Antimonial ores	3	80	{ 1·0 Borax 1·0 Sod carb.
Stanniferous ores	3	60	{ 2·0 Borax 4·0 Sod. carb.
Lead speiss	5	60	1·0
Blende	5	70	1·0
Slags	5	60	1·0
Brass and bronze	3	100	1·3
German silver	3	110	1·5
Copper	3	60	0·3

The scorifiers (Fig. 25) are made of best fireclay, and must withstand sudden changes of temperature and, to a certain extent, the corrosive action of molten lead oxide. The size of scorifiers used is governed by the size of the muffle, as it is desirable to make as many scorifications as possible at one time. If it is desired to mark them, red ruddle may be used, with which they are marked on the outer surface with numbers or streaks. The scorifiers, with contents, are placed, by

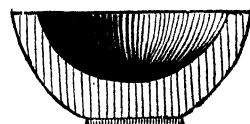



FIG. 25.

means of the tongs (Fig. 26) in the muffle, which should be at a bright red heat, and the door is closed.

A high temperature is especially necessary during the first or heating-up period if the material contains iron, zinc, tin, copper, or nickel and cobalt. After ten to fifteen minutes, the scorifiers have attained a bright red heat, the contents are molten, lead fumes are copiously given off, and a ring of molten slag rich in litharge appears; the muffle is then opened to admit air. During this second, or slagging, period, the current of air, passing continuously through the muffle, rapidly oxidises the material in the scorifiers; this oxidation is partly direct and partly brought about by the lead oxide, which acts on the undecomposed metallic compounds. Sulphur and arsenic are to a great extent volatilised, the metallic oxides and the gangue dissolve gradually in the molten litharge, slag and borax, and the noble metals are retained by the lead, which may also take up certain quantities of copper, tin, bismuth, iron, arsenic and antimony. While scorification is proceeding, the temperature of the muffle is somewhat lowered.

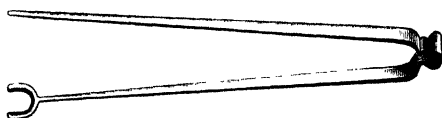



FIG. 26.

As scorification progresses, the slag ring gradually encroaches more and more on the surface of the lead button, until ultimately it closes completely over it. The muffle is then again closed, the temperature raised, so that the contents of the scorifier may become thinly fluid, and a small quantity (0·1 g.) of powdered anthracite is sprinkled over the surface; this reduces a little lead, which in turn cleans the slag, carrying the precious metals into the main button. After a further ten to fifteen minutes, the scorifiers are removed by the aid of scorifier tongs (Fig. 26) and the contents poured into moulds (Fig. 32, p. 109), which have been black-leaded and warmed.

When cold, the slag is removed from the lead button by hammering on an anvil, the lead beaten into the form of a cube, the edges and corners being blunted by gentle blows, and the cube cleaned by brushing. Should the lead appear to be brittle, owing to the presence of an appreciable amount of arsenic or antimony, it should not be directly cupelled (*cf.* Cupellation, pp. 110 *et seq.*); it is better, in such cases, to scorify again with an equal weight, or double the weight, of assay lead.

Lead buttons weighing more than 30 g. should preferably be rescorified in correspondingly small scorifiers, as the unavoidable loss

of silver on cupellation is then less than if directly cupelled. If, however, scorification is carried to an excessive point, too much lead oxidises and silver and gold pass into the slag.

If the material under treatment is so poor in silver that only a very small silver bead is obtainable from one lead button, concentration is resorted to, *i.e.*, the lead buttons from several scorifications are rescorified together, and this may be repeated until the silver, from a very considerable quantity of ore, has been collected into two lead buttons, each weighing 25 g. to 30 g. This is the method adopted, for example, with blister copper and other materials, usually very poor in silver.

(b) **The Pot or Crucible Assay.**—In this method the silver and gold from a large quantity of ore is collected in a lead button in one fusion and the button then cupelled. The method is particularly suitable for ores containing tellurium or horn silver, and also for very poor ores, slags, tailings and various residues and sweeps, especially when they contain carbonaceous material.

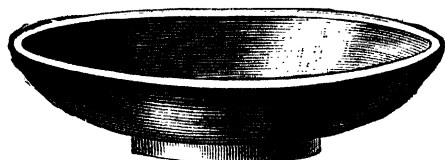



Fig. 27.

Tolerably smooth fireclay crucibles are employed for the fusion. The mixture of ore, etc., with litharge or red lead, fluxes, and reducing agent, generally with a piece of hoop iron also, is put into the crucible, and fused until the fusion is tranquil in a wind-furnace heated with charcoal or coke, the temperature being gradually raised, sometimes a gas- or oil-furnace is used. The silver content of the litharge or red lead must be taken into account and may easily be determined by fusing 100 g. of lead oxide with 1·5 g. charcoal powder and cupelling the resulting lead button.

The lead oxide decomposes any metallic sulphides, etc., and the metallic lead, reduced by the carbonaceous matter and sulphides collects the silver and gold.

Materials rich in sulphur, arsenic, antimony, or zinc, are preferably first roasted on roasting dishes or trays (Fig. 27), as otherwise appreciable quantities of silver may pass into the slag.

It is not possible to specify a fusion mixture equally suitable for all samples, although the following mixture will frequently be found satisfactory: 25 g. ore, 30 g. sodium carbonate, 40 g. red lead, and 1·5 g. charcoal are mixed in a mortar or on a mixing cloth and transferred to

a sufficiently large crucible and 10 g. of powdered borax glass put on the top. A piece of hoop iron is then inserted, the crucible covered with a lid and placed in the wind-furnace.

The heating must be gentle for the first quarter of an hour to produce incipient fusion or "fritting," otherwise the litharge is liable to melt and run down to the bottom of the charge, leaving the precious metals behind and causing a heavier loss in the slag. The damper is then drawn and the heating continued for about twenty minutes or until the fusions are tranquil. The iron strips are then removed, the crucibles withdrawn from the furnace with bent-nosed tongs, and the contents poured into moulds as before. After cooling, the lead buttons are removed, freed from slag by hammering, and brushed ready for cupellation (*cf.* Cupellation, pp. 110 *et seq.*). In some laboratories the crucible fusions are carried out in specially designed large muffle furnaces.

On mines where a large number of assays have to be made on the same class of material, it is usual to prepare a stock of mixed fluxes, made up in proportions to suit the character of the ore, but in many laboratories the nature of the ores to be assayed varies constantly, and the fluxes should then be made up specially. The following charges, given in grams and assay ton weights,[1] will be found useful:—

Table of Charges for the Dry Assay of Silver Ores in Grams.

	Siliceous.	Basic.	Pyritic.	Cupriferous Pyritic.
Ore	25	25	25	20
Red lead	30	30	40	60
Charcoal	1·5	2 to 3	...	...
Sodium carbonate . .	40	20	30	20
Borax	5	20	15	20
Sand	...	5	...	...

Table of Charges for the Dry Assay of Silver Ores in Assay Tons.

	Siliceous.	Basic.	Pyritic.	Cupriferous Pyritic.
Ore.	1·0	1·0	1·0	0·5
Red lead	1·0	1·0	1·25	2·0
Charcoal	0·05	0·06 to 0·1	...	...
Sodium carbonate . .	1·5	0·75	1·0	0·5
Borax	0·2	0·75	0·5	0·5
Sand	...	0·2	...	...

[*Note.*—Charges for ores containing stibnite, arsenical pyrites, cassiterite, tellurides, etc., are given under "Gold," pp. 133 *et seq.*]

[1] For explanation of assay ton weights, *cf.* p. 112.

With poor quartzose or similar material, up to 500 g. is taken for each melt. A good mixture consists of anhydrous sodium carbonate (one and a quarter to twice the weight of ore), 30 g. of red lead and 1·5 g. of powdered charcoal. The mixture is added gradually from a metal scoop (Fig. 28), or in a number of paper packets to avoid loss by foaming during the fusion, and borax, up to 25 per cent. of the weight of ore, is added, little by little. When the material contains an excessive amount of iron, more charcoal is needed for reducing ferric to ferrous oxide; otherwise none would be available for producing lead. Further, it is advantageous to sprinkle a mixture of litharge and argol (or a little granulated lead) on the tranquil surface of the fusion.

In the assay of lead slags (using 50 g. or more of material) with more protracted fusion with sodium carbonate, borax and argol, granulated lead is added, or may be sprinkled over the surface after fusion.

Rich lead ores are often assayed in thick wrought iron crucibles (*cf.* Lead assay, pp. 224 *et seq.*), and the lead button obtained is used

Fig. 28.

for the silver determination. In assaying poor lead ores from 15 to 20 g. of litharge is added to the ore and the whole treated as a silver ore by fusing with the flux and charcoal. The results of the pot assay are usually slightly higher than those obtained by scorification.

The residues from zinc distillation, which contain silver and lead, and as much as 30 per cent. of unburnt coal, may be treated as follows:[1]—Twenty grams of the coarsely powdered material is mixed with 50 g. of a mixture, containing 80 per cent. of potassium nitrate and 20 per cent. of sodium peroxide. The whole is introduced in quantities of from 3 or 4 g. at a time, into an iron crucible previously heated to redness, using an iron spatula. As soon as the first violent reaction is over, the crucible is put into a furnace and 60 g. of flux (consisting of fourteen parts of anhydrous sodium carbonate, eight parts of borax glass and two parts of argol) is added and heating continued until the fusion is tranquil; the charge is then poured into a warm iron mould (Fig. 32), and the cleaned button cupelled.

Details of laboratory crucible and muffle furnaces, together with specifications, have been given by G. T. Holloway.[2] These furnaces are shown in Figs. 29, 30 and 31.

[1] Sander, *Z. angew. Chem.*, 1902, **15**, 32 ; *J. Soc. Chem. Ind.*, 1902, **21**, 191.

[2] *Trans. Inst. Min. and Met.*, 1906-7, **16**, 341.

FIGS. 29 and 30.

In the assay of very rich ores, a notable amount of silver passes into the slag which must be re-treated after the lead buttons have been removed by hammering. The re-treatment consists in roughly

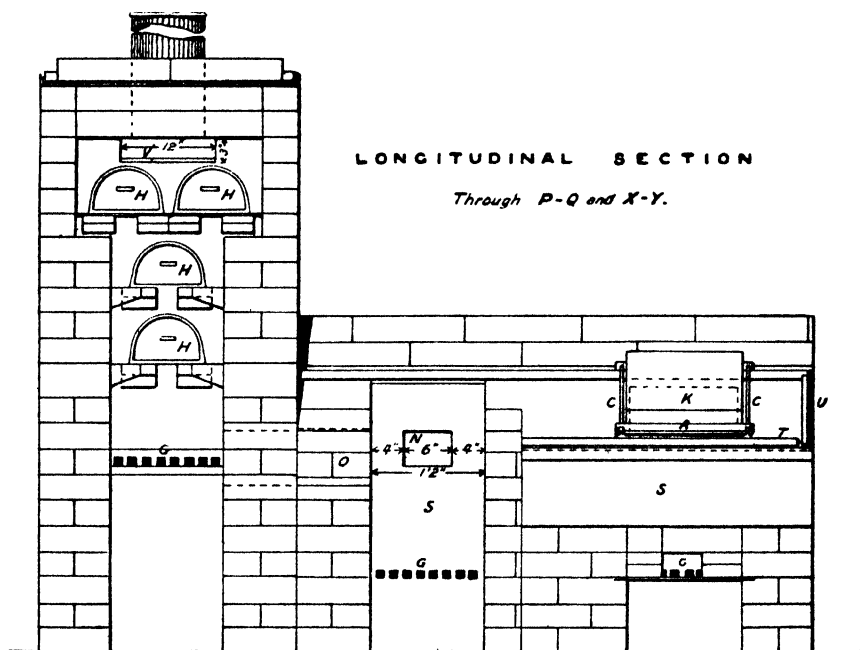



FIG. 81.

crushing the slag, mixing with a charge of borax, argol and litharge and fusing in the same crucible. If the lead buttons from the main

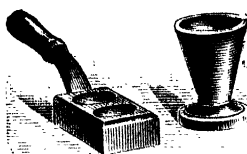



FIG. 82.

assay and the slag cleaning do not give a total weight of more than 30 g. they may be cupelled on the same cupel. If, however, the materials under investigation are poor, the loss of silver in the slag is negligible.

2. Cupellation.

The separation of silver and any accompanying gold from the lead obtained by scorification or in the pot assay is effected by oxidation of the base metal, on a cupel made of bone-ash, magnesia, or similar porous mixture (Fig. 33), at a bright red heat in a muffle furnace. As litharge is fluid at the temperature of cupellation the porous refractory cupel gradually absorbs the lead oxide formed, and finally a bright button of silver remains behind.

The burnt bone-ash, used for making cupels, is ground and sieved to about the fineness of wheat meal. After moistening with a little

FIG. 33.

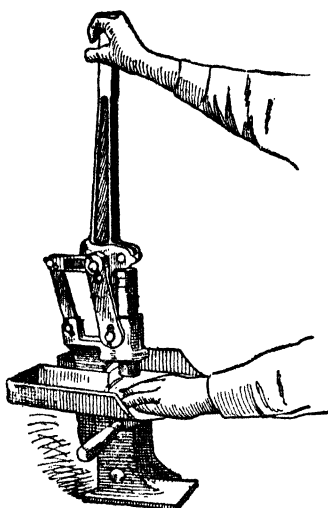



FIG. 34.

water, containing 2 per cent. of potassium carbonate, the bone-ash is shaped to the requisite form in a cupel mould, preferably of brass or gun metal. The cupels are kept on shelves in the furnace room and are thoroughly air-dried; they should be kept for several months before use. Cupels can also be made by means of a mechanical press (Fig. 34). Many brands of manufactured cupels such as Morganite and Mabor cupels are now on the market, and are largely used by assayers.

The ordinary cupel holds from 20 to 40 g. of lead, and is capable of absorbing all the lead oxide produced from this; larger cupels are sometimes employed, for instance, for lead containing but little silver.

Manipulation. The cupels are first gradually heated in the muffle, in order to drive off moisture and carbon dioxide completely. They should be placed well back in the muffle, in one or more rows, before

lighting up, and should be kept at a bright red heat for at least a quarter of an hour before use; otherwise the lead may spit on melting down on the cupel and so spoil the whole series.

After a thorough heating, the cupels are drawn forward, with iron tongs, and arranged in rows on the bottom of the muffle. The lead buttons, brushed, and blunted on the edges and corners, are carefully transferred to the cupels by means of the bent-nosed cupel tongs (Fig. 35), the front row being supplied first.

The muffle is then closed and the lead allowed to melt, when a dark skin first forms on the surface. As soon as this disappears and the molten lead, which acquires a bright convex surface, begins to give off lead fume, the muffle door is opened somewhat and cupellation proper commences.

The oxidation takes place rapidly. Drops of molten litharge form and, floating over the surface of the lead, are absorbed by the porous cupels. If the temperature is not too high, the lead smoke curls upwards and may produce a dark red crystalline and leafy deposit of litharge on the inner edges of the cupels (this deposit is yellow when

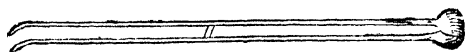



FIG. 35.

cold). At the same time, the drops of litharge on the convex surface of the lead unite together, forming a litharge edging to the lead.

When the muffle temperature is too high, this is indicated by the smoke rising vertically and no litharge ring referred to above will be formed. If the temperature is too low, the lead smoke keeps low over the cupels, which themselves appear somewhat dull; the temperature must then be immediately raised, otherwise " freezing " may take place.

As cupellation proceeds, the litharge drops gradually increase, and the fusing point of the alloy rises as it becomes richer in silver. The temperature becomes lowered by the continuous current of air passing into the muffle, so the door should be closed, and the temperature increased. Finally, the litharge drops disappear from the lead, as it gets smaller and smaller, a revolving iridescent skin of oxide is noticed for a short time, if the bead be not very small, and then suddenly the bead " brightens."

Cupels, containing very small silver beads, weighing only a few milligrams, may be removed from the muffle immediately after the beads have brightened; with larger beads, however, the cupels should be gradually drawn forward, to allow the silver to set slowly. If this be not done, there is a danger of silver being lost through "spitting" of the bead, owing to the sudden escape of absorbed oxygen through the prematurely formed solid crust. Objectionable spitting takes place

more frequently on bone ash than on Morganite or Mabor cupels. Beads, which have "spat," are often lighter than those which have not, and should not be taken into account in arriving at the result of the assay. By covering the cupels with hot inverted cupels slow cooling can be ensured, even when they are immediately removed from the muffle.

The small spherical beads and the larger hemispherical beads are removed from the cupels by means of pliers, squeezed to remove adhering particles torn from the cupel, well brushed on the under side with a stiff prill brush, and placed on a sheet of lead about the size of a playing-card and provided with a number of small depressions. The upper surface of beads from a thoroughly satisfactory cupellation is bright and of a whitish colour, the under side matt and silver-white. If "brightening" has taken place at too low a temperature in contact with litharge, the bead is matt and yellowish on its upper surface, owing to the presence of a thin film of oxide of lead; such beads are too heavy and must be rejected or re-cupelled with a small quantity of assay lead.

The beads never consist of absolutely pure silver; they contain from 0·2 to 0·3 per cent. of lead, with traces of copper. These impurities serve, to a certain extent, to compensate for the unavoidable loss of silver during cupellation.

Any gold and platinum contained in the material assayed is collected quantitatively in the silver bead and is determined therein (*cf.* Gold, p. 135).

The beads are weighed on a delicate assay balance (Fig. 23, p. 100).

When many assays of silver or gold ores have to be made, it is usual to work with "Assay Ton" weights. Since there are 32,666·6 oz. troy in a ton of 2240 lb., if the standard weight be made 32·66 g., each milligram of silver or gold obtained from this quantity will be equivalent to 1 oz. per ton. In the case of the short ton of 2000 lb., now largely used in many countries, the assay ton weight = 29·16 g.

Whenever these special weights are not used, the percentage value is first obtained, and from this the ounces, etc., per long or short ton can readily be calculated from the table on p. 113.

The individual beads obtained in assaying argentiferous lead ores usually agree well with each other in weight, but those from silver ores proper (especially native silver, silver glance or horn silver) frequently show appreciable variations, on account of the uneven distribution of the silver in the ore. It is then necessary to carry out a considerable number of assays and take the mean. Loss of silver occurs to a certain extent during slagging, in both the scorification and the pot assay, but the losses during cupellation are much greater, as silver is carried into the cupel along with the litharge, especially when very

porous cupels are used; further, some silver volatilises along with the lead. It is to be noted that if finished assays are left too long in the muffle, volatilisation of silver may take place.

When very great accuracy is desired in the assaying of ores, etc., the cupels are broken up and powdered and the lead reduced and cupelled (*cf.* Gold, p. 134); in this way most of the silver, etc., is recovered in the form of a weighable bead.

The silver in impure silver precipitates (chloride, iodide, or sulphide), such as are obtained in the extraction of low grade ores, burnt pyrites, etc., is best determined by scorification with lead, followed by cupellation of the button so obtained.

Table for computing the Troy Weight of Gold or Silver per Long and Short Ton.

Per cent.	Per ton of 2240 lb.			Per ton of 2000 lb.			Per cent.	Per ton of 2240 lb.			Per ton of 2000 lb.		
	oz.	dwt.	gr.	oz.	dwt.	gr.		oz.	dwt.	gr.	oz.	dwt.	gr.
0·0001	...	...	16	...	...	14	0·06	19	12	0	17	10	0
0·0002	...	1	7	...	1	4	0·07	22	17	8	20	8	9
0·0003	...	1	23	...	1	18	0·08	26	2	16	23	6	17
0·0004	...	2	15	...	2	8	0·09	29	8	0	26	5	0
0·0005	...	3	6	...	2	22	0·1	32	13	8	29	3	8
0·0006	...	3	22	...	3	12	0·2	65	6	16	58	7	0
0·0007	...	4	14	...	4	2	0·3	98	0	0	87	10	0
0·0008	...	5	5	...	4	16	0·4	130	13	8	116	14	0
0·0009	...	5	21	...	5	6	0·5	163	6	16	145	17	0
0·001	...	6	13	...	5	20	0·6	196	0	0	175	0	0
0·002	...	13	2	...	11	16	0·7	228	13	8	204	4	0
0·003	...	19	14	...	17	12	0·8	261	6	16	233	7	0
0·004	1	6	3	1	3	8	0·9	294	0	0	262	10	0
0·005	1	12	16	1	9	4	1·0	326	13	8	291	14	0
0·006	1	19	5	1	15	0	2·0	653	6	16	583	8	0
0·007	2	5	18	2	0	20	3·0	980	0	0	875	2	0
0·008	2	12	6	2	6	16	4·0	1306	13	8	1166	16	0
0·009	2	18	19	2	12	12	5·0	1633	6	16	1458	10	0
0·01	3	5	8	2	18	8	6·0	1960	0	0	1750	4	0
0·02	6	10	16	5	16	16	7·0	2286	13	8	2041	18	0
0·03	9	16	0	8	15	0	8·0	2613	6	16	2333	12	0
0·04	13	1	8	11	13	8	9·0	2940	0	0	2625	6	0
0·05	16	6	16	14	11	16	10·0	3266	13	8	2916	14	0

Combined Lead and Silver Assay.—The silver content of litharge scums, furnace hearth, and other oxidised products is determined by reducing the lead (*cf.* Lead assay, pp. 225 *et seq.*), and then cupelling. The lead buttons obtained from galena by fusion with sodium carbonate (*cf.* Lead assay, p. 224) are also cupelled to ascertain the silver content.

Plattner's quantitative blowpipe assay[1] is of special importance

[1] *Manual of Qualitative and Quantitative Analysis with the Blowpipe*, Plattner. English translation by H. B. Cornwall, 1902.

for prospectors; in sufficiently expert hands the method gives tolerably accurate results, working on small quantities of material (0·1 g.).

Combined Wet and Dry Silver Assay.—This method is particularly suitable for ores, mattes and alloys containing large quantities of copper. From 10 to 25 g. of the material to be assayed is treated with nitric acid, the whole heated until quite decomposed and taken up with water. A solution of 20 g. of lead acetate in water is then added, followed by a small quantity of sodium chloride solution to precipitate the silver and a portion of the lead present, while a further quantity of lead is frequently precipitated by the subsequent addition of sulphuric acid. The liquid is heated, then allowed to cool, filtered, and the residue and precipitate washed once with cold water. The filter paper and residue are dried, and the whole mixed with 25 g. of red lead, 20 g. of sodium carbonate, and 1·5 g. of charcoal. This charge is run down in a clay crucible as usual with a piece of hoop iron inserted in the charge, and the lead button cupelled.

Complete Analyses of silver minerals (ruby silver ore, silver glance, antimonial silver, stephanite, polybasite, tetrahedrite, etc.) are not required for technical purposes. If the silver only is to be determined, 1 g. of the powdered ore is dissolved in a mixture of nitric and tartaric acids (10 c.c. nitric to 2 g. tartaric acid), and the silver precipitated with hydrochloric acid. The precipitate is filtered off, washed with water containing a little nitric acid, until free from hydrochloric acid, and then dried in an air-bath. Fairly large quantities of silver chloride are weighed as such. The silver chloride is turned out on to glazed paper, the filter paper burnt, its ash transferred to a weighed porcelain crucible, treated with a few drops of nitric acid and, subsequently, a drop or two of hydrochloric acid, while it is heated on a water-bath; after the acid has been evaporated off, the bulk of the silver chloride is added, the crucible lid put on, and the crucible heated till the chloride begins to melt. Should the silver chloride amount to only a few milligrams or centigrams, however, the filter paper with the whole of the precipitate is dried, placed in a weighed Rose's crucible, the paper burnt, the crucible lid put on, the chloride reduced by heating for ten minutes in a current of hydrogen or coal gas, and the resulting silver weighed.

Electrolytic Methods[1] for the estimation of silver in ores are seldom used.

II.—The Assay of Silver Alloys

The poorer silver alloys are assayed in the dry way; the dry assay is frequently used for the richer alloys, as a preliminary determination to ascertain the approximate silver content previous to carrying out the determination in the wet way.

[1] *Cf.* Kiliani, *Berg u. Hütten. Zeit.*, 1883, **42**, 400.

A. Dry Assays

1. **Furnace Lead.**—If not very impure, the crude lead, obtained in the smelting of lead ores, may be directly cupelled in quantities of from 20 to 50 g. Should the impurities be considerable, the lead is first scorified with an equal or double weight of assay lead. Rich silver-lead is cupelled directly. Desilverised lead (soft lead) is cupelled in large cupels made to hold 100 g. of lead or first scorified in quantities of 100 g. and upwards, and the lead button of about 30 g., cupelled.

2. **Hard Lead** (antimonial lead) and the Mexican "Peñoles" lead, rich in silver and containing a considerable amount of antimony and arsenic, is first scorified with double its weight of assay lead, and concentrated if necessary by further scorification, and the resulting button is cupelled.

3. **Argentiferous Blister Copper and Refined Copper** require to be scorified with twenty times their weight of assay lead, and concentrated previous to cupellation.

4. **Silver Amalgam.**—Solid amalgam is heated very gradually on a cupel to a bright red heat in the course of an hour and a half, in a muffle, the cupel being covered with a second inverted cupel; the residue is cupelled with from six to eight times its weight of assay lead.

5. **Zinc Skimmings**, containing lead, zinc, and silver, from the Parkes desilverising process, are first scorified with sixteen times their weight of assay lead, and the button obtained is cupelled.

The following combination of wet and dry methods is described by L. Campredon.[1] A representative sample of 25 g. weight is dissolved in a mixture of nitric and tartaric acids, the silver and a considerable quantity of lead precipitated with hydrochloric acid, and the washed and dried precipitate fused with the addition of 20 g. of litharge and the necessary flux; the button of lead thus obtained is cupelled.

6. **Crude Silver** (containing 95 to 96 per cent. of silver), **Refined Silver** (containing 97 to 99·5 per cent. of silver), and **Cement Silver** are assayed by wet methods only (*cf.* pp. 117 *et seq.*).

7. **Bullion and Silver containing Copper.**—Before the introduction of the Gay-Lussac wet method of assay, these alloys, even those richest in silver, were assayed exclusively in the dry way by taking an accurately weighed amount (two quantities each of 0·5 g.), and cupelling with a sufficiency of assay lead on a cupel of pure bone-ash.

The unavoidable loss during cupellation was carefully determined by introducing check assays into the muffle, and by making corrections for these losses, the actual fineness could be arrived at with tolerable accuracy. The carefully weighed check assays mentioned above were

[1] *Guide pratique du Chimiste Métallurgiste et de l'Essayeur*, 1898.

made up to contain approximately the same amount of silver and copper as the assay pieces under test. They were placed in different parts of the muffle, generally one on each line, and their position in the muffle was taken into account in calculating the losses on the assays.

Preliminary Assay. As the amount of lead needed depends on the percentage of copper and other metals (other than silver and gold) in the alloy, the approximate fineness is first ascertained either by the touchstone, or by cupelling 0·1 to 0·2 g. with eighteen times its weight of assay lead.

Streaks are made with the alloy on a touchstone of black basaltic stone, and, adjoining these, other streaks are made with test needles of known fineness; by a comparison of the colours, after treatment with acid, an approximate result is arrived at. The presence of zinc in silver alloys considerably affects the streak, and gives rise to high results.

It is possible to ascertain by means of the streak whether an alloy contains silver or not. The streak is treated with one or two drops of pure concentrated nitric acid, and, when it has disappeared, leaving no trace of turbidity, a drop of hydrochloric acid produces the characteristic white precipitate, or a turbidity, if silver is present. Lead may also give a turbidity, but this disappears on the addition of a little water.[1]

Alloys poor in silver (400/1000 and under) require eighteen to twenty times their own weight of assay lead for cupellation; alloys of approximately 500/1000 require sixteen, 700/1000 require twelve, 800/1000 require ten, 900/1000 require eight, and 950/1000 and over require four times their own weight. In mint laboratories this assay lead is kept in standard lumps or pellets.

The Assay Proper. From two to four cupels are placed in the muffle and heated to cupellation temperature, the assay lead introduced, and the muffle closed; as soon as the lead has "uncovered," the alloy (0·5 g. if fine silver, or 1 g. if 800/1000), wrapped in sheet assay lead, and check are added with the aid of tongs, and the muffle again closed. After about a couple of minutes, when complete fusion has taken place, the muffle is partly opened, and cupellation proceeds. The litharge ring appears gradually, but seldom litharge crystals. Finally, the bead becomes iridescent, and brightens. The finished assay is allowed to cool slowly to obviate spitting, and shortly after setting (dropping of the surface) it is removed from the muffle. The beads are removed with sharp-nosed pliers, squeezed, brushed on the under side, and placed on a black wooden board, provided with a number of small depressions, ready for weighing on the assay balance. Instead of adding

[1] *Cf.* The distinction of silver and imitation silver alloys, p. 128.

the alloy to lead in a cupel it may be wrapped in the proper amount of assay lead and introduced at once into the hot cupel.

The amount of loss noted on the checks is added to the weights of the assay beads and the fineness is calculated from this corrected figure.

Assays of upper and lower portions of ingots, owing to segregation, may show differences up to three-thousandths in fineness between 980 and 725, and considerably more between 400 and 200.

This determination of the fineness gives reliable results and also serves as a preliminary to the more accurate volumetric determination by the Gay-Lussac method (cf. *infra*). It is suitable in particular for the assay of low-grade and impure silver alloys of commerce.

B. Wet Assay for Silver Alloys

The two methods which are almost exclusively used for the wet assay of silver alloys are the sodium chloride method of Gay-Lussac[1] and the ammonium thiocyanate method of Volhard.[2] The gravimetric determination by precipitation of silver chloride, which takes longer than the volumetric method, is seldom used in practice when only the silver content is in question; it is, however, employed in Indian mints,[3] where, owing to the high temperature prevailing and the consequent evaporation of the standard solutions, these cannot be kept at a constant working value.

Electrolytic methods of deposition have not hitherto been introduced, as they do not offer any advantages.

1. Gay-Lussac's Sodium Chloride Method.

This method is employed in most mint laboratories. A solution of the alloy is made in nitric acid and adjusted to contain slightly over 1000 mg. of pure silver. The silver is precipitated in the cold by means of a solution of pure sodium chloride (100 c.c. of "standard salt solution"), not quite sufficient to precipitate the whole of the silver; the solution is cleared by shaking, and the silver remaining in solution is precipitated by successive additions of 1 c.c. of a "decimal salt solution," shaking well after each addition, until no further turbidity is produced with salt solution.

[1] *Instruction sur l'Essai des Matières d'Argent par la Voie humide*, Paris, 1833.

[2] *Die Silbertitrierung mit Rhodanammonium u. s. w.*, 1878, previously published in the *Berg u. Hütten. Zeit.*, 1875, **34**, 83; 1876, **35**, 333 (Lindemann); *J. prakt. Chem.*, 1877 [2], **15**, 191.

[L. Campredon, in his *Guide pratique du Chemiste Métallurgiste et de l'Essayeur*, calls this the method of Charpentier, who published the principle of the method in the *Comptes rend.* in 1871.]

[3] For a detailed description, see *The Indian Mint Assay of Silver Bullion*, by F. T. C. Hughes, *Trans. Inst. Min. and Met.*, 1907-8, **17**, 334.

The solutions required for the determination are:—

1. *Standard Salt Solution.* This is made by dissolving 5·416 g. of pure sodium chloride in 1 litre of distilled water at 15°.

[If the solution is required for frequent use, it is as well to prepare, say, 50 litres at a time, starting with a cold saturated solution of pure salt, of which 100 c.c. contains 31·84 g. of sodium chloride between 10° and 20°. A solution of ordinary common salt may be freed from calcium sulphate and magnesium chloride by treating it with barium chloride and sodium carbonate, filtering, boiling down, and recrystallising the salt thus obtained.]

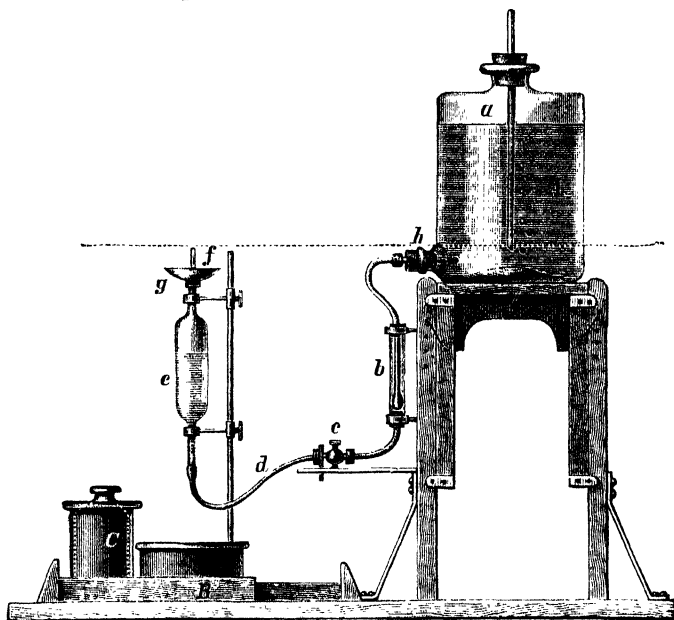



Fig. 36.

One hundred c.c of this solution will precipitate just 1000 mg. of silver; as a little more than this quantity is present in the assay, the precipitation is completed with salt solution of one-tenth the strength. From 5 to 10 litres of this standard salt solution is stored in a bottle, supported on a firm wooden stand and provided with a side tubulure near the bottom. The Stas pipette, which has a capacity of exactly 100 c.c., and is a simplification of the Gay-Lussac pipette, is filled from this bottle as shown in Fig. 36.

2. "*Decimal*" *Salt Solution*, made by diluting 100 c.c. of the standard solution No. 1 to 1 litre.

3. "*Decimal*" *Silver Solution.* This is made by dissolving 1 g. of chemically pure silver in 6 c.c. of pure nitric acid (sp. gr. 1·2) and diluting to 1 litre.

Both these dilute solutions are kept in glass-stoppered bottles. The approximate silver content of the alloys under examination must be ascertained by a preliminary assay in the dry way, or by Volhard's volumetric method (p. 122).

In mint-prepared alloys (made from silver of known fineness and pure copper), the silver content is already known and merely requires to be checked by the sodium chloride method.

First, the titre, or standard value, of the standard salt solution (which should be at a temperature of as near 15° as possible), is fixed by means of a nitric acid solution of 1·003 g. of chemically pure silver. The silver, in the form of clippings, is treated in a 200 c.c. shaking-bottle with 14 c.c. of pure nitric acid (sp. gr. 1·2), and gently heated in a water-bath until dissolved; when solution is complete, the bottle is placed on a metal guide immediately under the Stas pipette (Fig. 36), which is filled with the standard salt solution (No. 1), and closed at the upper end by means of the finger. In the London mint, a hot-plate covered with asbestos is used in place of a water-bath, and a series of six pipettes is arranged, which are filled by means of a foot pedal. The solution in the pipette is run into the bottle, which is then closed with its numbered stopper and shaken for five minutes, in such a way that the contents are thrown violently against the sides of the bottle. In doing this, the bottle must be firmly gripped, the forefinger being pressed against the stopper.

The silver chloride clots and settles rapidly; any particles remaining attached to the sides or to the stopper can be detached by sloping and rotating the bottle. After a minute or two, 1 c.c. of the "decimal" salt solution (No. 2) is run in from a pipette, the latter being allowed to touch the inner side of the neck of the bottle. If silver still remains in solution, a turbidity is observable near the surface of the liquid when the flask is held to the light, and this spreads through the whole liquid on gently shaking.

The number of cubic centimetres of "decimal" salt solution added is marked with chalk on a board, hung up in a convenient position, and divided for the various numbered bottles. The bottle is shaken until clear and the addition of "decimal" salt solution continued, 1 c.c. at a time, until no further turbidity is to be seen. The final cubic centimetre, which shows no turbidity, is not counted, and the previous cubic centimetre is counted as a half only, the corresponding chalk-mark being crossed.

For example, suppose the third addition shows no turbidity, the amount of salt solution used for the complete precipitation of 1003 mg. of silver = 100 c.c. of "standard" solution is equivalent to 1000 c.c. of "decimal" solution + 1·5 c.c. of "decimal" solution, or altogether 1001·5 c.c. of "decimal" salt solution.

In practice, the thickness of the cloud produced by the addition of the first cubic centimetres is used to indicate the probable amount required.

If an alloy on preliminary dry assay, reckoning also the cupellation loss, shows a fineness of 734/1000, the amount to be taken for the wet assay is arrived at as follows:—

734 mg. Ag are contained in 1000 mg. alloy.
Then 1003 " " " x "

$$\therefore \quad x = \frac{1000 \times 1003}{734} = 1366 \text{ mg.}$$

Consequently, 1366 mg. is weighed out, dissolved in 10 to 12 c.c. of nitric acid (sp. gr. 1·2), free from chlorine, and the solution treated exactly as described above.

Assuming that the fourth cubic centimetre is the first to show no turbidity, the amount of salt solution = 1000 + 2·5 = 1002·5 c.c. of "decimal" salt solution. Since 1001·5 c.c. = 1·003 g. silver, the sample under examination (1366 mg.) contains 1004 mg. silver, which corresponds to a fineness of 735 per 1000.

Remarks.

1. *Apparatus.* The simple and cheap Stas pipette is a perfectly satisfactory substitute for the original Gay-Lussac pipette. It must be protected from dust, and, if a few drops of the "standard" solution should overflow on to the sides of the pipette, it should be washed with strong sodium hydroxide solution (it must be remembered that 0·1 c.c. of "standard" solution = 1 mg. Ag). In mint laboratories a special stand is used, to allow of several bottles being immersed at the same time in the copper water-bath. For the simultaneous shaking of from ten to twelve samples, a shaking apparatus as shown in Fig. 37 is used. The individual bottles must be firmly fixed and the glass stoppers well secured.

2. *Effect of Foreign Metals, etc.* Black particles, remaining behind on dissolving the alloy, may contain gold, platinum, carbon, or silver sulphide. The latter dissolves on continued warming, with addition of 1 to 2 c.c. of strong nitric acid. Turbidity, due to the presence of antimony, disappears on the addition of tartaric acid, which should also be added if bismuth is present. Alloys containing mercury, according to Debray, should be heated gradually in a small graphite crucible in a muffle to the melting point and the button then dissolved in nitric acid.

The presence of lead and tin,[1] according to Kerl, necessitates the use of sulphuric acid as solvent in place of nitric acid; traces of lead, however, do not interfere.

[1] *Cf.* Salas, *Trans. Amer. Inst. Min. Eng.*, 1912, 267.

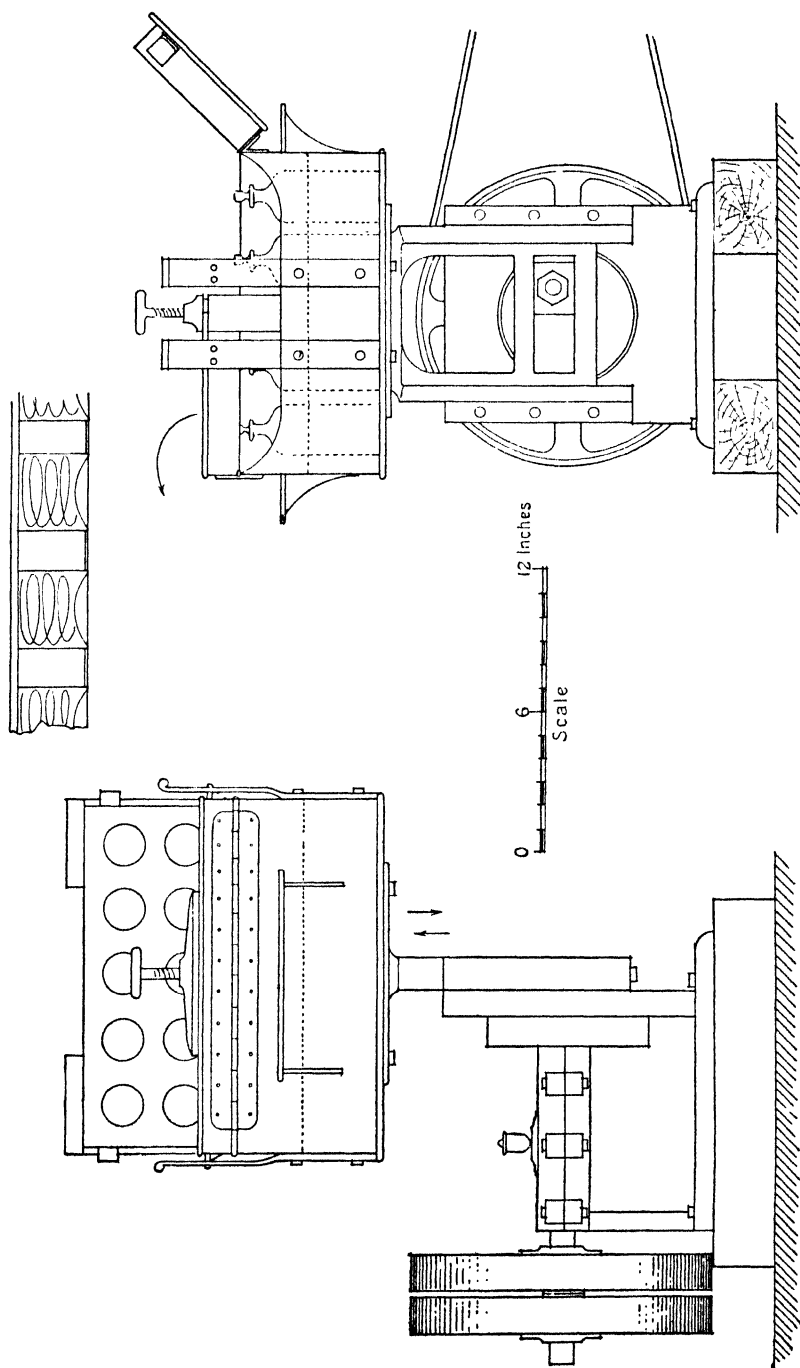



Fig. 37.

3. *Action of Silver Chloride.* Investigations by Mulder show that silver chloride is slightly soluble in the sodium nitrate produced during titration, and that, on precipitation of the silver with the calculated quantity of sodium chloride, about 0·5 mg. of silver remains in solution; consequently an excess of 0·5 c.c. of "decimal" salt solution is really used, when the addition of this is continued to the point of complete disappearance of turbidity. This has, however, no influence on the result of the assay, since it occurs to the same extent in standardising with pure silver, as in the assay itself.

4. *Accuracy of the Assay.*[1] The fineness is usually expressed in thousandths; expert assayers can determine the end-point of precipitation to 0·1 mg. by making smaller additions of the "decimal" salt solution than 1 c.c.

Stas (1865) found that the accuracy was about 1 part in 100,000 when every precaution was taken, and has given particulars of how this degree of accuracy was obtained.[2]

Hoitsema[3] worked to obtain the highest degree of accuracy, and states that "The accuracy of this determination is of the order $1/10^6$—that is, one part in one million." These results were obtained on fine silver.

2. Volhard's Ammonium Thiocyanate Method.

This method depends on the precipitation of silver from nitric acid solution by means of a solution of ammonium or potassium thiocyanate, in presence of ferric sulphate as indicator. The curdy precipitate of silver thiocyanate, which is but little affected by light, is insoluble in cold dilute nitric acid; the slightest excess of the precipitant is shown by the persistent red coloration, due to the formation of ferric thiocyanate.

The solutions needed for the determination are:[4]—

1. *Ammonium Thiocyanate Solution.* This salt can be obtained chemically pure and is more suitable than the potassium salt, which frequently contains chlorine. Seven and a half to eight grams is dissolved in water and the solution made up to 1 litre. This is standardised by titrating 50 c.c. of silver solution (No. 2) diluted with 100 to 200 c.c. of water in a beaker, 5 c.c. of a cold saturated solution of iron alum, free from chlorine, being added; the end-point is indicated by a permanent pale brownish red colour. The thiocyanate solution is then diluted so that 1 c.c. is exactly equivalent to 0·01 g. Ag; the value must, of course, be checked by several titrations.

[1] *Cf.* Dewey, *Ind. Eng. Chem.*, 1913, 5, 209.
[2] *Les Lois des Proportions chimiques*, Brussels, 1865, pp. 39-48.
[3] *Dutch Mint Report*, 1903.
[4] *Cf.* R. Fresenius, *Quantitative Analysis*, 7th edition, vol. ii., pp. 361 *et seq.*; also, E. A. Smith, *Trans. Inst. Min. and Met.*, 1906-7, 16, 154.

By diluting 100 c.c. of the solution to 1 litre, a "decimal" thiocyanate solution is obtained (1 c.c. = 1 mg. Ag); this solution is employed towards the end of the titrations.

2. *Silver Solution.* Ten grams of chemically pure silver is dissolved in 160 c.c. of pure nitric acid of sp. gr. 1·2, in a long-necked flask, care being taken to avoid loss by spitting; the nitrogen oxides are completely driven off, and the solution, after cooling, is diluted to 1 litre. One c.c. of this solution contains exactly 0·01 g. Ag.

3. *Solution of Iron Alum.* A saturated solution free from chlorine is used, of which 5 c.c. is added in each titration. Any yellowish colour in this solution is destroyed by the addition of a little colourless nitric acid or ferric nitrate solution may be used.

To carry out the determination, from 0·5 to 1 g. of the sample in the case of alloys is dissolved in 10 to 20 c.c. of nitric acid (sp. gr. 1·2), in a beaker covered with a clock-glass, and heated on a sand-bath until nitrous fumes have disappeared. The cover and the sides of the beaker are then washed with water, 100 to 150 c.c. of water and 5 c.c. of the iron alum solution added, and the solution titrated, the beaker being placed on a sheet of white paper. If preferred the titration may be carried out in a white-glazed porcelain basin.

When the titration approaches completion, the iron coloration disappears only slowly on shaking or stirring; the "decimal" thiocyanate solution is then used for finishing the determination.

Remarks.—The solutions must be titrated cold; nitric acid does not interfere, but any nitrous acid must be previously removed by boiling.

The presence of gold in the sample (as, for instance, in crude silver and refined silver) is shown on solution in nitric acid; the dark brown or black powder left as a residue is washed with hot water by decantation, collected in a small crucible, dried, heated, and weighed (*cf.* Assay of Gold, Silver, and Copper Alloys, p. 147).

In the presence of high percentages of copper (above 70 per cent.), the end-point is not sharp, and an accurately measured quantity of the silver solution (No. 2) is then added to the strongly coloured solution, or a corresponding quantity of pure silver may be added, so that the ratio Cu : Ag = 7 : 3, is not exceeded.

Mercury must be previously removed from the alloy by heating to a temperature of about 700°.

The presence of palladium causes high silver results to be obtained.

Arsenic, antimony, tin, zinc, cadmium, lead, and bismuth do not interfere with the titration; cobalt and nickel have an effect similar to that of large quantities of copper, on account of the colour of their solutions.

A. E. Knorr[1] recommends a combination of the Gay-Lussac and Volhard methods, viz., the precipitation of the greater part of the silver with salt solution, and titration of the remainder with ammonium thiocyanate.

3. Gravimetric Determination of Silver.

The precipitation of silver as chloride has been already mentioned (p. 117). The following gravimetric method, in which the silver (even when present in minute quantities) is determined as iodide, is very accurate. Hampe, after careful investigation,[2] strongly recommends the method as described by R. Benedikt and L. Gans[3] for the determination of silver in its alloys with lead. The process is as follows:—

The amount of the alloy to be taken varies from 10 g. to several hundred grams, according to the richness of the lead in silver; it is dissolved in dilute nitric acid (free from chlorine) with addition of tartaric acid if antimony is present. The quantity of nitric acid is so regulated, that there is an excess of about 10 c.c. The clear solution (filtered if necessary) is considerably diluted to 300 c.c. or to several litres, and excess of potassium iodide solution is added, but too great an excess should be avoided; the containing vessel is then covered and heated. The lead iodide dissolves, reacts with the nitric acid, and iodine is set free. Heating is continued until the iodine is volatilised and the liquid colourless. The silver iodide is filtered off and weighed; or it can be converted into chloride and weighed as such.

Benedikt examined poor leads, the silver contents of which were very carefully ascertained in the dry way to be 0·003 per cent. and 0·0006 per cent. respectively. By his method, using 147 g. and 239 g. of material respectively, he found 0·0034 and 0·00054 per cent. of silver.

Hampe checked the method by precipitation of minute quantities of silver, in presence of considerable amounts of chemically pure lead nitrate (320 g. of lead nitrate, 1 mg. of silver as silver nitrate, 2 litres of water, and 10 c.c. of nitric acid, precipitation being effected by 0·5 g. of potassium iodide in aqueous solution). The result obtained was 0·98 mg., instead of 1 mg.

The method is especially suitable for the examination of assay lead, litharge, and red lead, which are intended for dry assay work.

The Examination of Bar Silver (Crude and Refined Silver, Fine Silver, Cement Silver).—A complete analysis is seldom required. It is usual to determine the gold left on dissolving a fairly large quantity of the sample (10 g. or more) in dilute nitric acid (*cf.* Gold, p. 148), then the silver in an aliquot part of the solution, either by the Gay-Lussac

[1] *J. Amer. Chem. Soc.*, 1897, **16**, 814.
[2] *Chem. Zeit.*, 1894, **18**, 1899; *J. Soc. Chem. Ind.*, 1895, **14**, 304.
[3] *Chem. Zeit.*, 1892, **16**, 4, 12.

or Volhard method, or gravimetrically, and finally an examination is made for impurities, more particularly bismuth, a small amount of which has the effect of producing hardness and brittleness in silver alloys (*e.g.*, coinage alloys).

The presence of antimony and tin may be recognised by qualitative tests; a few grams of the alloy dissolved in pure nitric acid shows a whitish turbidity when these metals are present; copper gives a blue coloration with excess of ammonia, lead and bismuth being at the same time precipitated as hydroxides.

Platinum and the platinum metals are almost always present, but usually only in traces. H. Rössler has frequently found palladium in refined silver; weighable quantities colour the nitrate solution yellowish.

Sulphur is determined by heating a considerable quantity of the sample, in the form of drillings, in a current of chlorine. This is conveniently effected in a long porcelain boat, placed in a hard glass tube. The volatile chlorides are collected in a receiver containing water acidified with hydrochloric acid, and the sulphur is precipitated as barium sulphate. In this way bismuth, tin, arsenic, and antimony can also be separated from silver by the volatilisation of their chlorides; copper, lead, and iron remain in part with the silver chloride and partially in the cooler portions of the glass tube beyond the boat.

Selenium is frequently found in certain classes of silver, and according to Debray it may be determined as follows:—About 100 g. of the silver is dissolved in nitric acid (sp. gr. 1·3), the gold removed by decantation, the silver precipitated with hydrochloric acid, and the filtrate evaporated to dryness. To convert the selenic acid to selenious acid, the residue is boiled with hydrochloric acid continuously for a quarter of an hour, and the selenium precipitated, as a red powder, by addition of a solution of sulphurous acid. The precipitate is transferred to a weighed filter paper, washed well with water, the filter paper and its contents dried for from three to four hours in an air-bath at 100°, and weighed.

Determination of Silver in Plating Solutions (Silver Baths).— Silver baths usually contain from 4 to 20 g. of silver, as silver-potassium cyanide, and from 10 to 50 g. of potassium cyanide per litre together with potassium cyanate and potassium chloride and a little copper, zinc, and nickel as impurities. Cadmium is frequently added to these baths as cadmium potassium cyanide, since the plating produced tarnishes less readily than a pure silver deposit.

For the analysis, 10 c.c. of the solution is placed in a covered porcelain dish, 10 c.c. of hydrochloric acid added, and the whole heated on a water-bath in a fume cupboard for fifteen minutes; the cover is then removed and washed, and the contents of the dish

evaporated to dryness on the water-bath. The presence of a small quantity of copper is indicated by a brownish colouring of the residue, due to anhydrous copper chloride. The dry mass may either be treated by scorification followed by cupellation, or digested with 25 c.c. of water and a few drops of nitric acid, the residue filtered off after cooling, washed with water containing nitric acid, dried in an air-bath, incinerated in a Rose's crucible, whereby a considerable amount of silver chloride is reduced, then strongly heated for five to ten minutes in a current of hydrogen or coal gas, and any carbon subsequently burnt off.

As an alternative method the solution may be evaporated to dryness in a small dish made of assay lead and then the whole scorified and cupelled.

These methods are also suitable for the assay of cyanide solutions obtained during the extraction of silver by cyaniding.

Any copper contained in the filtrate from the silver chloride, which usually amounts to a few milligrams, may be precipitated with sulphuretted hydrogen, the precipitate collected on a small filter paper, washed with water containing a drop of sulphuric acid and a few cubic centimetres of sulphuretted hydrogen solution, dried, and roasted in a porcelain crucible (finally over a large Bunsen flame) to cupric oxide: $CuO \times 0{\cdot}7989 = Cu$.

If cadmium is also present, both metals are precipitated as sulphides; the washed precipitate is then washed off the filter paper into a porcelain dish and boiled for five to ten minutes with dilute sulphuric acid (1 : 5), whereby the cadmium sulphide is completely dissolved (A. W. Hofmann's method). The copper sulphide is treated as described above. The cadmium is precipitated again as sulphide, from the largely diluted solution, collected on a tared filter paper, the free sulphur extracted by washing with alcohol and then with carbon disulphide after which the precipitate is dried at 100°, and weighed, after being allowed to cool for half an hour. $CdS \times 0{\cdot}7781 = Cd$. It is, however, preferable to treat the sulphide with nitric and sulphuric acids and weigh as sulphate. $CdSO_4 \times 0{\cdot}5392 = Cd$ (*cf.* Cadmium, p. 307).

The potassium cyanide content of baths is most rapidly determined by titration with silver nitrate solution (*cf.* Vol. I., p. 627).

Recovery of Silver from Silver Chloride and Silver Thiocyanate.—Silver chloride is boiled repeatedly with dilute hydrochloric acid, washed thoroughly with water by decantation, and dried; it is then mixed with half its weight of anhydrous sodium carbonate and one-eighth its weight of potassium nitrate, and the mixture gradually introduced into a roomy clay crucible placed in a wind-furnace, and heated until the fusion is tranquil; the slag is poured off

and the metal cast in a warm ingot mould, or granulated by pouring in a thin stream into water, which is kept in agitation. The ingots are cleaned with hot dilute sulphuric acid.

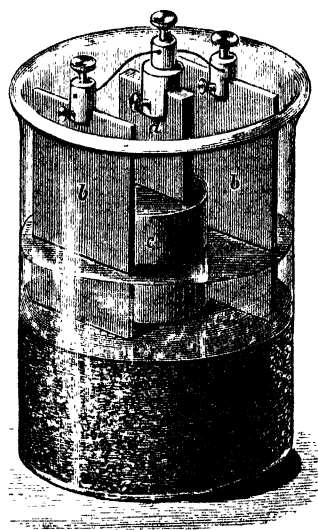
At the Paris mint one hundred parts of silver chloride are run down with seventy parts of chalk and four parts of powdered wood charcoal.[1]

Silver chloride may also be reduced by treatment with pieces of pure zinc in the presence of water slightly acidified with sulphuric acid; the spongy silver obtained is treated with hot dilute sulphuric acid to dissolve the remaining zinc, washed well with water, dried, and melted down with nitre and borax glass.

Pfeiffer[2] prepares pure silver by the electrolytic decomposition of silver chloride in a porous porcelain cell, as follows:—A strip of platinum foil or a rod of iron is surrounded by well-washed silver chloride, moistened with dilute sulphuric acid, in a porous cell; the cell is placed in a glass battery jar containing dilute sulphuric acid, with a thick cylinder of amalgamated zinc round the cell. The zinc and platinum poles are then connected up. After reduction, the spongy silver is repeatedly washed, and then either melted down or worked up directly to silver nitrate.

FIG. 88.

An almost identical method had previously been described by Priwoznik.[3] Instead of the platinum used by Pfeiffer, two silver strips are employed. Water slightly acidified with sulphuric acid is poured into a porous cell, 27 cm. in height and 8·5 cm. wide (*c*, Fig. 38), and two heavy zinc rods, or a thick zinc plate, *a*, are introduced and connected by copper wire with two silver strips, *b*, each 12 cm. wide. The latter stand in silver chloride moistened with sulphuric acid (1 : 10), contained in a glass jar 32 cm. high and 22 cm. in diameter. The porous cell also stands in the silver chloride. The amount of silver chloride contained in the jar corresponds to about one kilogram of silver. The zinc plates require frequent cleaning.

Pure silver (assay silver) is prepared electrolytically in this way in

[1] Kerl, *Metallurgische Probierkunst*, 2nd edition.

[2] *Chem. Zeit.*, 1898, **22**, 775; *J. Chem. Soc. Abstr.*, 1899, **76**, 366.

[3] *Oesterr. Zeitschrift. f. Berg. u. Hüttenwesen*, 1879, 418; Balling, *Fortschritte im Probierwesen*, 1887, pp. 18, 19.

the mints at Vienna, Sydney, Melbourne, etc., from the silver nitrate solution obtained in gold parting after inquartation.

To obtain silver chloride from silver thiocyanate, von Juptner recommends boiling it with three to five times its volume of hydrochloric acid, nitric acid being added, drop by drop, until the red coloration at first produced disappears. The silver chloride is then washed, dried, and treated as described above.

The Distinction of Silver from Imitation Silver Alloys.—The streak on the touchstone is tested by treating it with a drop of nitric acid and adding a minute quantity of hydrochloric acid to the solution so obtained (*cf.* p. 116).

Imitation alloys, base coins, etc., are cleaned with soap and rubbed on a moistened spot with a stick of silver nitrate; a heavy black stain is at once noticeable when an alloy of base metals is so treated. This is the method frequently employed in banks.

Silver and silver-plated goods, when treated with a cold saturated solution of potassium bichromate in nitric acid of sp. gr. 1·2, immediately show a cherry-red stain of silver chromate, which does not wash off. Should there be a suspicion that the goods are plated, the upper layer is removed on one part, and the bared metal, which is frequently of a different colour, is treated with bichromate solution. The red stain is not produced on German silver, brass, tombac, etc.

Thin plating may be recognised, according to R. Finkener, as follows:—The article to be tested is cleaned with alcohol and ether, to remove lacquer, and then treated with a 1·5 per cent. solution of yellow sodium sulphide, obtained by boiling a solution of 30 g. of crystallised sodium sulphide in 10 c.c. of water for ten minutes with 4·2 g. of flowers of sulphur, and diluting to a litre. After contact with this solution for ten minutes, the article is washed with water.

Silver shows an even steel-grey stain; imitation alloys, at best, show a ring darkened at the edges.

As amalgamated copper behaves in much the same way as silver under this treatment, it is well to heat the article first and so remove any mercury which might be present. This alloy, however, is rarely met with.

GOLD

Native gold, all gold ores and commercial products, most gold alloys and sweep from these, usually contain silver in varying amounts. As a rule, therefore, in the assay of these materials, the gold and silver are obtained as an alloy, which is then subjected to the operation of parting.

The dry assay of ores, etc., is, with few exceptions, identical with the dry silver assay: viz., scorification, or pot assay, followed by cupellation of the lead button. The wet and dry methods are sometimes combined.

The high value of gold, and the consequent effect of differences in the assays, render especial care necessary in taking representative samples. This is somewhat complicated by the fact that the gold mostly exists in ores as native gold and is very unevenly distributed. The same holds good for gold sweep from alloys, which often have to be assayed. Further, ingots of gold alloys are not entirely uniform throughout.

Gold Ores.

The most important sources of gold are :—

Native Gold, with 0·16 to 38 per cent. silver (Electrum), usually also some copper and iron.

Gold Amalgam and *Gold-Silver Amalgam*, containing respectively up to 39·5 per cent. gold and 36 per cent. gold, with 5 per cent. silver.

Palladium Gold, with 86 per cent. gold, 4·1 per cent. silver, and 9·8 per cent. palladium.

Rhodium Gold, with 57 to 66 per cent. gold and 34 to 43 per cent. rhodium.

Bismuth Gold, with 64·5 per cent. gold.

Very frequently gold ores contain *Tellurium;* such ores are found more particularly in the Siebenbürgen, in Colorado and in Western Australia.

The following minerals may also be mentioned :—

Petzite ($x\ Ag_2Te + Au_2Te$), containing 3·3 to 25·6 per cent. gold and 40·8 to 46·8 per cent. silver.

Sylvanite, *Calaverite* ($x\ AuTe_2 + AgTe_2$), containing 26·5 to 40·6 per cent. gold and 2·24 to 11·3 per cent. silver.

White Tellurium, or *Krennerite*, containing 24·9 to 29·6 per cent. gold, 2·7 to 14·6 per cent. silver, and 2·5 to 19·5 per cent. lead.

Foliated Tellurium, or *Black Tellurium* (*Nagyagite*), containing 5·9 to 7·6 per cent. gold, and 57·2 to 60·5 per cent. lead.

Tellurium Silver (*Hessite*), Ag_2Te, often contains gold.

Iron pyrites, copper pyrites, arsenical pyrites, mispickel, etc., contain small quantities of gold.

I.—Methods of Ore Assay

1. Dry Assays.

As the method to be employed in the dry assay of gold depends largely on the character of the ore, it is advisable to carry out a preliminary examination by mechanical and chemical means.

Simple washing methods are particularly valuable for this preliminary examination. The apparatus used is either a wooden pan (Figs. 39 and 40), or an iron or wooden dish called the Batea (Fig. 41), or flat porcelain dishes or plates.

The material, in a fine state of division, is shaken with water on the pan (Fig. 39), and the muddy water carefully poured off, so that the residue forms a thin mud. The pan is then held horizontally, gentle end taps are given to it, and at the same time it is moved sideways, the action being similar to that in mechanical concentrators. After a short

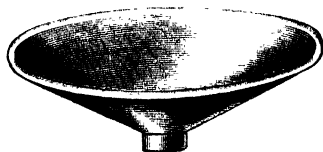



Fig. 39. Fig. 40. Fig. 41.

time the different constituents of the ore separate according to their specific gravities. Porcelain dishes are manipulated in much the same way. By rejecting the apparently non-metallic products, adding fresh material and repeating the operations, an enrichment of the heavy products is ultimately attained. A zone of more or less finely-divided gold cannot always be detected with certainty, for some ores, as, for instance, the Transvaal conglomerates, contain most of the gold in an extremely fine state of division, in tiny microscopic leaflets, and much of this passes off with the finest of the mud in the process of washing.

Other accompanying minerals, such as pyrites, etc., are, however, easily visible, and small quantities of these can then be examined before the blowpipe. Tellurium-gold and tellurides (see above) must be carefully looked for; these may easily be mistaken, when in a finely-divided state, for mispickel or arsenical pyrites. The tellurides, on gently warming with 1 c.c. of concentrated sulphuric acid in a test tube, give a cherry-red solution; the colour disappears on heating more strongly.

A more delicate test consists in heating the ore with nitric acid, diluting somewhat, filtering, evaporating the filtrate with sulphuric acid until dense fumes are evolved, and then adding tin foil. The same carmine colour is produced. In both these tests the presence of iron interferes with and often completely masks the colour due to tellurium.

An excellent test consists in heating the ore in a current of chlorine,[1] the ore being contained in a glass tube, the end of which is bent and made to dip into hydrochloric acid. The temperature required is below dull redness, and the chlorine should be passed for about one hour. The hydrochloric acid solution thus obtained is diluted, nearly neutralised with sodium carbonate or ammonia, and saturated with sulphur dioxide while still warm. The tellurium often takes some hours for complete precipitation, and the solution should, therefore, be left in a warm place over night.

The distillation in chlorine may be obviated by fusing the ore with sodium peroxide in a nickel, iron, or copper crucible, boiling with water, filtering, neutralising with hydrochloric acid, and passing in sulphur dioxide as above. Selenium is precipitated, as well as tellurium, by both these methods; the former, however, is soluble in potassium cyanide solution, and may thus be separated and reprecipitated as a red powder by acidifying the solution with hydrochloric acid and heating. For a quantitative determination of tellurium in an ore, the chlorine distillation method may be recommended.

When the Batea (Fig. 41) is used for the preliminary treatment of the ore, the specifically lighter portions of the powdered ore are removed by a circular and sloping motion; the heavier particles form a tail on the lower portion of the pan.

(*a*) **Scorification Assay.**—The silver scorification assay (pp. 102 *et seq.*) is, as a rule, also applicable to gold. The process is particularly used for rich gold ores not containing tellurium, for all ores containing lead and those rich in copper, furnace products, and sweep.

The quantities of assay lead and borax required are discussed on p. 103.

In carrying out the scorification assay, it is very frequently necessary to "concentrate," *i.e.*, the lead buttons from a number of scorifications are united and scorified together, and so on, until finally, on cupellation, a sufficiently large bead of silver and gold is obtained.

(*b*) **Pot Assay** (*cf.* Silver, pp. 105 *et seq.*).—This process is eminently suited to many auriferous materials, and is very largely used; larger amounts of ore can be taken (up to several hundred grams), and consequently the effect of an uneven distribution of the gold on the assay is decreased.

The fusion is effected in smooth-walled crucibles, either in an

[1] Holloway and Pearce, *Trans. Inst. Min. and Met.*, 1907-8, 17, 171.

ordinary wind furnace or in one fired with gas or oil. Details of the charges for simple ores (flux, reducing material, litharge, red lead, etc.) are given in the section on the Silver Assay (pp. 105 *et seq.*).

In America and South Africa the pot assay is frequently performed in muffle furnaces, whereby a more uniform heating of the crucibles is attained. From six to eight crucibles are put into the muffle at one time, the ore charge being from 20 to 100 g.

According to Mitchell, with rich material containing 5 to 10 oz. of gold per American ton (2000 lb. avoirdupois), 1 assay ton (29·166 g.) should be taken; with poor material, 2 to 4 assay tons, and for very rich ores, half an assay ton.

A satisfactory charge is:—For 1 assay ton of ore, 1 assay ton of sodium carbonate, 1 of red lead, 0·25 of borax glass, and 0·05 of charcoal. The fusion is carried out in a wind-furnace, the temperature being gradually increased by regulating the damper; towards the end a fairly high temperature should be attained. The crucible, on being taken from the furnace, is gently tapped on the furnace plate and allowed to cool, or, preferably, the contents may be poured at once into a warm iron mould (Fig. 32, p. 109); one crucible will then serve for five or six fusions.

The slag from the fusion of very rich ores is run down with 25 to 30 g. of red lead, 1 to 2 g. of charcoal powder, and a little sodium carbonate, and the resulting lead button cupelled.

Ores containing much sulphur, arsenic, or antimony, are subjected to a preliminary roasting, first alone, and finally, after admixture with a little charcoal powder or anthracite, in fire-clay roasting dishes or sheet iron trays, washed over with fire-clay or ruddle. To prevent loss of gold, the temperature must be raised very gradually. W. Witter has proved that pyritic ores roasted with this precaution suffer no loss of gold; he has also pointed out that ores containing small quantities of tellurium or mercury must undergo a more protracted roasting at a low temperature before heating more strongly.

For the assay of mint sweep, etc., the following method will be found to be very satisfactory. A sample of 500 g. is taken, and the moisture first determined. The dried sample is then passed through an eighty mesh sieve, and the metallic particles are collected, weighed, and assayed separately. Of the fine material, 25 g. is thoroughly roasted and mixed with 60 g. of red lead, 1·5 g. of charcoal, 30 g. of sodium carbonate, and 30 g. of borax, and fused in a crucible in the usual way. The button of lead obtained should weigh about 30 g.; if the material is rich, the slag is re-fused with the addition of 20 g. of red lead and 1 g. of charcoal; a second lead button is thus obtained. The lead buttons are then cupelled separately and parted in the usual way or may be scorified together before cupellation.

In assaying roasted pyrites, enough charcoal powder must be used to reduce the ferric oxide to ferrous oxide, and the latter must be slagged off by means of a sufficient amount of borax or powdered glass. If too little charcoal powder is used, the red lead or litharge is not reduced. When the fusion has become tranquil, a little red lead mixed with charcoal and flux may be thrown in to carry down any prills suspended in the slag. Witter states that it is not advisable to assay more than 200 g. of material in one fusion, otherwise lower yields are obtained than if a number of fusions of 100 g. each are carried out.

The methods to be used in the assay of complex gold ores vary with the nature of the associated minerals. General instructions for their treatment have been given by E. A. Smith.[1]

Arsenical ores, as already stated, require a preliminary roast to remove the arsenic. One assay ton of ore is placed on a roasting dish in a cool muffle, and roasted carefully at a low temperature at first, stirred frequently, and the temperature gradually raised. When no incandescent particles are visible, the temperature is raised to full redness. After a time 1·5 to 3 g. of powdered anthracite is mixed in and the whole again roasted at a full red heat.

When there is no further smell of arsenic or of sulphur, the roast is mixed with the following charge and fused down in the usual way:—red lead 1, charcoal 0·1, sodium carbonate 0·75, borax 0·25 assay tons.

Antimonial ores[2] are best treated by a fusion method in which sufficient nitre is added to the charge to oxidise the stibnite partially, the remainder being oxidised by the red lead, which at the same time forms a lead button to carry down the precious metals. The amount of nitre necessary must be determined by experiment, the object being to obtain a soft lead button weighing 25 to 30 g. The following is a useful charge for average ores:—

	Assay Tons.
Ore	1·0
Red lead	2·0
Sodium carbonate	0·75
Borax glass	0·2
Nitre	0·5 to 0·75

In the event of antimony being reduced and alloying with the lead the resulting button will be hard, and it should be scorified with the addition of assay lead before being cupelled.

Telluride ores[3] are best treated by crucible assay in which an excess of red lead is used. A moderately hot fire is required for the

[1] "The Assaying of Complex Gold Ores," *Trans. Inst. Min. and Met.*, 1901-2, **9**, 315.
[2] Kitto, *ibid.*, 1906-7, **16**, 89.
[3] Holloway and Pearce, *ibid.*, 1907-8, **17**, 171; *cf.* also, S. W. Smith, *ibid.*, p. 463.

fusion, but great care is necessary to avoid excessive heating at the commencement. Owing to the corrosive action of litharge on the crucibles used, an addition of burnt fire-clay to the charge is found to be most useful, and is preferable to sand.

The following is a useful average charge for telluride ores:—

	Assay Tons.
Ore	1·0
Red lead	1·0 to 4·0
Charcoal	0·05
Sodium carbonate	1·0
Borax	0·5
Burnt fire-clay	0·5

The amount of red lead required varies with the amount of tellurium present, the more tellurium the greater must be the excess of red lead used and a portion of this should be placed as a cover on the bulk of the charge.

Large buttons from this fusion may be scorified before being cupelled, but then the operation must not be carried so far that the lead is covered with slag or tellurium passes from the slag into the lead button.

Auriferous tinstone[1] should be assayed by the crucible method; an excess of red lead and sodium carbonate is desirable. The following charge will be found to give good results, even with dressed tin ores carrying gold:—

	Assay Tons.
Ore	1·0
Red lead	2·0
Charcoal	0·05
Sodium carbonate	1·5
Borax	0·25

(*c*) **The Cupellation of the Auriferous Lead** (*cf.* Silver, pp. 110 *et seq.*).—Lead buttons from the pot assay, when the slag is difficult to remove, are re-melted for a short time on scorifiers; the slag is then easily removed from the buttons by hammering and brushing. Hard, impure lead buttons are scorified with assay lead before cupellation.

Towards the end of the cupellation of auriferous lead, the temperature should be raised as in the silver assay. Beads rich in gold do not "spit."

There is a distinct loss of gold by absorption during cupellation. To recover the gold from the cupels, the portions not saturated with litharge are removed, and the rest is treated as follows:—One hundred parts of cupel substance are fused in a crucible with seventy-five parts

[1] Bannister, *Trans. Inst. Min. and Met.*, 1905-6, 15, 513.

of fluor spar, seventy-five of sand, one hundred of sodium carbonate, fifty of borax, and two of powdered charcoal. The lead button obtained is then cupelled.

(*d*) **Parting.**—The beads are weighed on an assay balance and then parted by means of nitric acid or concentrated sulphuric acid. Complete separation is only attained if the ratio of gold to silver is 1 : 2·5 or 1 : 3 and above (*cf.* p. 140).

Alloys of forty parts gold and sixty parts silver are so white that they cannot be distinguished in appearance from silver; an alloy of seventy parts gold and thirty parts silver has a pale brass-yellow colour.

To effect the "parting" a white bead is flattened out on a polished anvil and treated in a test tube or small porcelain crucible with a few cubic centimetres of pure nitric acid (sp. gr. 1·2 to 1·3), free from chlorine, and the contents heated to boiling. If the button disintegrates and the gold separates as a black powder, more silver is present than is actually necessary for the parting. Boiling is continued as long as coloured nitrous fumes are given off; the acid is then carefully poured off, the residue is washed repeatedly by decantation with distilled water, and the gold dried, either on the water-bath or in an air-bath, and finally heated gradually to redness. The black powder turns yellow and becomes somewhat coherent. After cooling, it is brushed on to the balance pan and weighed. The silver is ascertained by difference.

A white bead which turns brown and is attacked only on the surface by nitric acid, does not contain sufficient silver for parting. Such a bead must be washed, dried by heating, wrapped in lead foil with two or three times its weight of assay silver in small pieces, and the whole placed on a heated cupel and cupelled, an operation which takes only a few minutes to perform; yellow or yellowish beads are treated similarly, without first testing with nitric acid.

Direct melting of the bead with the inquartation silver is simpler; this is done in a hole in a piece of charcoal or on a cupel before the blowpipe. The flattened bead is parted with nitric acid as explained. If the parting is effected with concentrated sulphuric acid, a denser yellow residue of gold is obtained, and platinum and traces of lead remain with the gold, whereas small quantities of platinum are dissolved from the alloy, if nitric acid is used in the parting. The detection of platinum and the solubility of silver-platinum alloys is dealt with on p. 146.

When the relation of gold to silver in the bead is 1 : 2·5 or 1 : 3, boiling twice with nitric acid is sufficient for complete parting, and the bead retains its original shape, which is an advantage inasmuch as less loss occurs in washing and collecting, than when the gold is in a finely divided condition.

Plattner's blowpipe assay for gold[1] is specially useful to prospectors. It consists of a crucible assay or scorification assay, concentration, and cupellation. Since only small quantities of material can be used (100 mg. for each assay), the material is previously enriched as far as possible by panning (*cf.* p. 130). The tiny gold beads are measured with a scale.

2. Extraction Assays for Ores.

From time to time it is necessary to examine ores in the laboratory in order to ascertain the method of treatment most suitable for the extraction of the gold on a large scale. At the present time the most important methods of treatment are by amalgamation and by the cyanide process, and it is advantageous to examine ores to find out whether they are amenable to treatment by these methods and what losses of gold and reagents are likely to be met with in actual practice.

For the amalgamation assay, 100 to 500 g. of the crushed ore is ground with water in an iron mortar or a mortar amalgamator, sufficient water being added to form a thick cream-like pulp. About 50 g. of clean mercury is then added and thoroughly incorporated, the mixture being well stirred from time to time for several hours. Water is then added to dilute the pulp and the whole gently stirred to allow the amalgam to settle to the bottom. The tailings are then washed from the amalgam and are collected in a suitable receptacle, dried and assayed. The amalgam is also collected, squeezed through chamois leather and the hard amalgam thus obtained gently heated in a covered porcelain crucible to drive off the remaining mercury. The residue is weighed, cupelled with lead, the remaining bead weighed, recupelled with lead and silver if necessary, parted, and the gold obtained washed, heated and weighed.

From the original assay of the ore, the assay of the tailings and the weight and nature of the bullion obtained, valuable information may be acquired.

Similarly, extraction experiments with solutions of potassium cyanide may be useful. The ore is treated with dilute solutions containing 0·5 per cent. or less of potassium cyanide, for varying lengths of time, the solution filtered and assayed for gold, free cyanide and alkalinity. For gold, the solution is mixed with pure litharge, evaporated to dryness on the water-bath, and then run down with the usual fluxes in a crucible, and the lead button cupelled. Evaporation to dryness of the auriferous cyanide solution in a small lead dish, followed by scorification and cupellation, may also be adopted. The residues from the cyanide extraction are also assayed for gold. Further tests may also be made after the addition of an alkali if necessary.

[1] Cf. *Manual of Qualitative and Quantitative Analysis with the Blowpipe*, Plattner; English translation by N. B. Cornwall, 1902.

For the determination of gold in dilute cyanide solutions produced on a large scale,[1] the following method has been found satisfactory. Two hundred and fifty cubic centimetres of the solution is placed in a beaker, 4 g. of zinc shavings and 30 c.c. of 20 per cent. lead acetate solution added, and the whole boiled for one minute; 30 c.c. of concentrated hydrochloric acid is then added to dissolve the zinc, and when all action has ceased, the solution is boiled and allowed to stand until cool. The clear liquor is decanted, the residual spongy lead collected, squeezed into a ball, wrapped in lead foil, dried, cupelled with a little silver, and parted in the usual way.

The Detection of Minute Quantities of Gold.—The roasted ore is shaken with an alcoholic solution of iodine; the solution is then absorbed by a few strips of Swedish filter paper, and, after drying and incinerating these, the presence of gold is indicated by the purple colour of the ash (Skey).

A delicate reaction consists in treatment with bromine water, concentration of the solution by evaporation, and addition of stannous chloride, whereby a precipitate of purple of Cassius is produced.

Carnot's colorimetric gold assay[2] depends on the production of a rose to purple tint in a hydrochloric acid solution containing gold, by the addition of zinc dust, in the presence of arsenic acid and ferrous chloride. Standard solutions are used containing gold varying from 1 mg. per 100 c.c. to 1 mg. per 1000 c.c. Details of this method and of Rose's colorimetric stannous chloride method are given by T. K. Rose.[3]

Mayençon[4] states that a very delicate method of detection consists in the electrolytic deposition of the gold on a platinum wire.

T. Döring[5] recommends the following method for the detection of small quantities of gold in ores:—One hundred grams of the finely powdered ore is slightly but evenly moistened with 1 to 2 c.c. of a mixture of about equal volumes of bromine and ether, by shaking the ore for at least a couple of hours with the solvent in a stoppered bottle. During this time the interior of the bottle must appear well filled with bromine vapour. Subsequently, 50 c.c. of water is added, and the mixture digested for a couple of hours, with occasional shaking. The whole is then filtered, and the clear solution evaporated to about one-fifth its volume; a little bromine water is added, to cause the formation of a little stannic chloride, which is necessary for the production of the purple tint, and the solution is then treated with stannous chloride

[1] For the methods of examination of cyanide solutions from gold cyaniding works, *cf. The Chemistry of Cyanide Solutions*, by J. E. Clennell, 1904.

[2] *Cf.* Weill, *L'Or*, 1896, p. 378; *Berg u. Hütten. Zeit.*, 1896, **55**, 215; *J. Soc. Chem. Ind.*, 1896, **15**, 674.

[3] *The Metallurgy of Gold*, by T. Kirke Rose, 6th edition, 1915, pp. 65, 521; *cf.* also, *Chem. News*, 1892, **66**, 271.

[4] *Berg u. Hütten. Zeit.*, 1887, **46**, 403.

[5] *Ibid.*, 1900, **59**, 49, 73, 97.

in a narrow test tube, and the colour observed. A 0·1 per cent. gold solution shows at once a deep brownish violet coloration, which is opaque, even in thin layers. In a solution containing 0·01 per cent. of gold, an immediate brownish violet colour is produced, and a 14 cm. deep column is opaque. With 0·001 per cent. of gold, an immediate pale violet tint results, which increases in depth after a few minutes; a 14 cm. column is transparent. With 0·0005 per cent. of gold, the stannous chloride shows, after several minutes, especially in thicker layers, a pale violet-red colour, which gradually becomes more intense. Solutions containing 0·0001 per cent. of gold require to be first evaporated to about one-fifth of their volume; a drop of bromine water is then added, after which the addition of stannous chloride will show a distinct rose tint in a 14 cm. column. Solutions containing 0·00005 per cent. of gold, treated similarly, show a very faint but still recognisable rose tint in a column 14 cm. deep. The colorations produced by the very weak solutions, can be detected with greater certainty, if compared with a 14 cm. column of pure water in a test tube. The method as described is applicable to (*a*) pure quartzose ores; (*b*) impure quartz, especially if containing iron; (*c*) pyritic ores, even when containing antimony and arsenic; when notable quantities of sulphur, antimony, or arsenic are present, the ore should be roasted previous to extraction; (*d*) good results can be obtained with ores containing sulphides of other heavy metals, for instance with galena, zinc blende, and copper pyrites; but these ores should be subjected to a preliminary roasting. With ores containing copper pyrites, a certain amount of cupric bromide goes into solution during extraction, and on subsequent addition of stannous chloride a white crystalline precipitate of cuprous bromide is produced; but as this is white, it does not interfere to any extent with the observation of the purple coloration. The method is not applicable with any certainty to ores containing tellurium, as the ethereal bromine mixture dissolves tellurium, tellurous acid and tellurium gold; stannous chloride then produces a black precipitate of tellurium which may completely conceal the purple coloration produced by the gold.

By means of the Döring method, it is possible to detect the gold in ores containing 0·5 g. per ton (about 8 grains per ton).

Gold in Electro-plating Baths.—In gold baths, which contain a large quantity of potassium cyanide besides gold potassium cyanide, the gold is estimated as follows:—Fifty cubic centimetres is treated with 30 c.c. of 25 per cent. hydrochloric acid in a 500 c.c. porcelain dish, in a draught chamber. The dish, covered at first with a clock-glass, is warmed on a water-bath, at the end of ten minutes the cover-glass removed, the solution evaporated down to about 20 c.c., a hydrochloric acid solution containing 5 g. of stannous chloride added,

and the heating continued for a further quarter of an hour; 100 c.c. of water is then added, the whole filtered through a strong (or double) filter paper, the residue washed on the filter paper with boiling water, and any residue adhering to the dish removed with a piece of moistened filter paper and added to the rest. The filter is dried, burnt in a porcelain crucible, and the residue fused with 5 g. of granulated assay lead, the button thus obtained being cupelled. If the gold button is not a full yellow, it contains silver, and is parted according to the directions given on p. 135.

Instead of taking up the "purple of Cassius" precipitate with lead, it may be strongly heated by itself in a porcelain crucible, and then warmed on a water-bath with 5 c.c. of hydrochloric acid and 0·5 c.c. of nitric acid, the crucible being covered at first with a watch-glass. The solution obtained is evaporated, taken up with water containing a little hydrochloric acid, filtered, and the gold precipitated with ferrous sulphate, instead of with oxalic acid, on account of the copper usually present. The precipitate is filtered through a double ash-free paper, washed, dried, burnt in a porcelain crucible, and the pure gold weighed.

The potassium cyanide content of baths is either determined volumetrically, according to the method described in Vol. I., p. 627, or 1 c.c. of the solution is diluted with 20 c.c. of water, silver nitrate added in excess (equivalent to 0·1 or 0·2 g. silver), the solution stirred, 5 c.c. of nitric acid (sp. gr. 1·2) added, and the whole allowed to stand for several hours. The precipitate is then filtered, washed, and dried, the filter and its contents heated in a porcelain crucible and the carbonaceous matter burnt off; after a final strong heating, the auriferous silver is weighed. The gold contained in 1 c.c. of bath solution is deducted. $KCN = Ag \times 0{\cdot}6035$.

Gold baths usually contain from 1 to 3 g. gold, and from 5 to 20 g. potassium cyanide per litre. When gold chloride is used for the preparation of the bath, instead of the double cyanide, this potassium cyanide determination comes out somewhat too high, on account of the silver cyanide precipitate containing silver chloride.

II.—The Assay of Gold Alloys

The materials for assay are chiefly rich gold bullion, which contains but little silver, copper, and platinum metals, alloys of gold with copper (coinage alloys), gold with silver, gold with silver and copper; industrial alloys of low standard containing up to 10 per cent. of zinc, amalgams, auriferous platinum, and gold-platinum alloys (*cf.* Platinum, p. 154), auriferous lead, bismuth, antimony, and alloys of more or less indefinite composition resulting from the treatment of scrap, lemel, sweep, etc.

Parting with Nitric Acid. Inquartation with Silver.—The parting of beads obtained in ore assays is described on p. 135. Alloys of gold with silver and copper are also usually parted with nitric acid.

If the gold is alloyed with an excess of silver, or if the alloys contain much copper or other base metals, the gold remains behind as powder after treatment of the alloy with hot nitric acid.

The approximate gold content of rich alloys is ascertained by a preliminary assay, and then a gold-silver alloy is made, in which the relation of gold to silver is 1 to 2·5 or 1 to 3 (hence the term "inquartation"). A strip is then rolled out and made into a loose spiral, which is boiled in a parting-flask with pure nitric acid, until the silver is completely dissolved out; the porous gold is washed with hot distilled water, transferred to a small unglazed annealing cup, dried and ignited, and the pure gold weighed.

When, as in gold-copper coinage, the gold content of the alloy is known, and only requires to be checked, the silver-gold alloy is obtained on a cupel in the muffle by direct cupellation with the calculated amount of silver for inquartation and the necessary quantity of lead.

A. Preliminary Assay

1. Alloys which do not contain Copper.

Touchstone Assay.—The streak produced on a touchstone is compared with those of "needles" of known fineness.

Concentrated nitric acid should not dissolve the streak completely, and the gold should remain undissolved; this forms a method of distinction from imitation gold alloys.

Alternatively the bead obtained by cupellation of the original gold-silver-copper alloy with assay lead (*cf.* 2, Cupreous Alloys) is compared with those obtained from standard alloys containing 600, 700, 800, 900 thousandths of gold, and with a bead from pure gold, all fixed on a white card and surrounded with a black edging.

When the percentage of silver reaches 56, the gold content cannot be judged from the colour; such alloys are white; 2 per cent. of silver will change a gold-coloured alloy to a brassy colour.

Full yellow alloys require two and a half to three times their own weight of silver, light yellow alloys twice their weight, and white alloys their own weight. As an example, suppose that by comparison with standard beads, the gold content of the alloys is estimated at between 700 and 800 thousandths, the amount of silver required for the usual assay weight of 500 mg. is calculated as follows:—Anything between 700 and 800 is taken as 700; consequently, in 500 mg. of the alloy,

there are $0{\cdot}7 \times 500 = 350$ mg. of gold and 150 mg. of silver. Now 350 mg. of gold require $3 \times 350 = 1050$ mg. of silver; 150 mg. of silver are already present in the alloy, so that 900 mg. of assay silver must be weighed out and cupelled with the alloy. Should the original estimate have been too low, and the gold be exactly 800 per 1000, the amount of silver taken, 900, would still be ample for parting, since the relation of gold to silver would be 400 to $(900+100)$ or 1 to 2·5. Usually the inquartation silver used is two and a half times the weight of the gold.

The gold content of white alloys which are alloyed with an equal weight of silver cannot be approximately gauged in the manner described, and coherent gold is obtained on parting only when the gold content of the original alloy is not much under 500 per 1000. Otherwise the gold remains as a powder and requires more care in decantation and collecting.

2. Alloys which contain Copper.

For alloys that contain no silver, the touchstone assay is applicable, needles consisting of gold-copper alloys of known composition being employed. Even small quantities of silver, zinc, etc., in the gold-copper alloy, however, have quite an appreciable effect on the colour of the alloy.

The usual preliminary assay consists in cupelling from 250 to 500 mg. of the alloy with eight to twenty-five times its weight of assay lead, according to the amount of copper present, as in the silver assay (p. 110), except that a somewhat higher temperature must be employed, because copper is more difficult to oxidise completely in presence of gold. The loss in weight gives the amount of copper and other base metals, and, by comparison of the bead with standard beads, the quantity of inquartation silver required for the assay proper is ascertained.

B. The Assay Proper

Cornet Assay.—The method presupposes an approximate estimation of the gold, silver, and copper by a preliminary assay, and varies in minor details in nearly every laboratory.[1]

Two portions of exactly 500 mg. each, consisting of flattened pieces or drillings (from the upper and lower parts, if from ingots), are weighed out on a sensitive balance, and the requisite quantity of silver for inquartation added;[2] the mixtures are wrapped in pure lead foil,

[1] *Cf.* Claudet, *Trans. Inst. Min. and Met.*, 1906-7, **16**, 136.
[2] *Cf.* E. A. Smith, *J. Inst. of Metals*, 1910, **3**, 105.

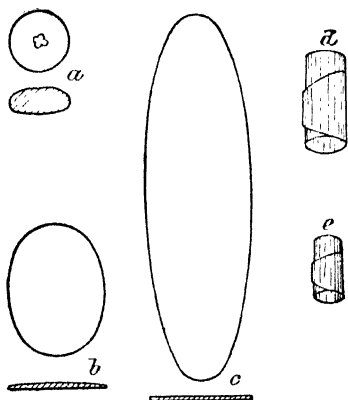
and are put, with the necessary number of units of assay lead, on to a small tray and taken to the muffle furnace, containing a number of heated cupels. The lead is put into two cupels in the centre of the muffle and allowed to melt and "uncover" in the closed muffle; the small lead packets containing the sample and silver are then introduced, the muffle closed until cupellation begins, when it is again opened and the operation carried out, as in a silver assay (p. 110). Litharge crystals should not appear. A higher temperature must be employed than in the silver assay, owing to the higher melting point of the gold-silver alloy. The maintenance of the proper temperature during cupellation has a considerable influence on the results.

J. Prinsep, as long ago as 1828, made use of silver-gold and gold-platinum alloys for controlling the furnace temperature. Since the introduction of the Le Chatelier thermo-electrical pyrometer (see Vol. I., pp. 156 *et seq.*), it has been possible to fix the proper temperature for the assay of gold alloys by accurate experiments. T. Kirke Rose has published the results of a complete series of experiments for this purpose.[1] He concludes that the mean temperature of the muffle during cupellation should be 1060° to 1065°; each 5° above this means a loss of gold to the extent of 0·01 per 1000.

FIG. 42.

The assays, after they have "brightened," are drawn forward in the muffle, and after setting, whereby a slight sinking of the surface takes place, they are removed altogether. The beads are detached by fine-nosed pliers, brushed on the under side, well squeezed with the pliers, and brushed again until the under surface is clean. The beads are then flattened on an anvil with a polished steel hammer, and the flattened bead heated to redness in the muffle on a piece of porcelain, and rolled out. No cracks should show at the edges on rolling. The rolled pieces are annealed, numbered by stamping, rolled on to a thick glass rod, and the cornets then slacked out.

In the London Mint, where 500 mg. of gold ingot, 1100 mg. of silver (960 fine) and 4 g. of lead are taken, the beads, rolled to a thickness of a visiting card and a width of 6 to 9 mm., have a length of about 25 mm.

The accompanying illustrations[2] (Fig. 42) show the bead *a;*

[1] *J. Chem. Soc.*, 1893, **63**, 707. *Cf.* also, *The Metallurgy of Gold*, T. K. Rose, 6th edition, 1915, pp. 535 *et seq.*, and *J. Soc. Chem. Ind.*, 1893, **12**, 359.

[2] From Rose's *Metallurgy of Gold*, 6th edition, p. 535.

flattened bead, *b*; rolled strip, *c*; cornet, *d*; and annealed cornet, after parting, *e*, all in natural size, as obtained at the London Mint from 500 mg. gold, etc.

The cornets are now boiled in a parting-flask with nitric acid. The parting flasks are long-necked flasks of well annealed potash glass (or Jena glass), about 200 mm. in length, 50 mm. wide in the body, and 20 mm. wide at the end of the neck. Twenty c.c. of pure nitric acid of sp. gr. 1·2, free from chlorine, nitrous acid, and selenic acid is introduced into each flask. Each is placed on a stand (Fig. 43) over a rose-burner, and the acid is heated nearly to boiling; the cornets

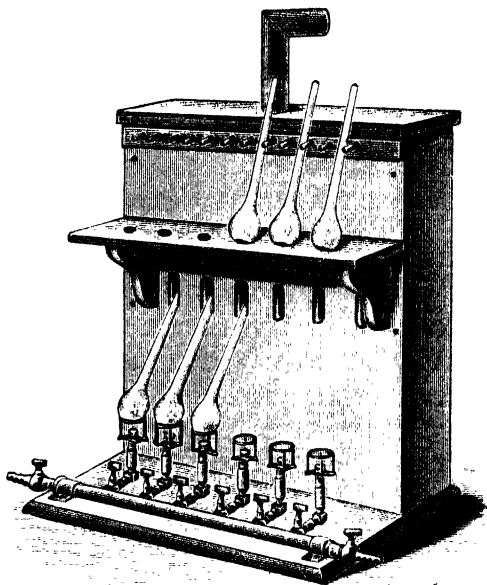



FIG. 43.

are introduced, and boiling is continued for ten minutes after nitrous fumes have disappeared.

The flasks are removed from the stand with a cork-lined spring clamp, the acid carefully poured off into a porcelain vessel, and the cornets washed by decantation with hot distilled water; about 20 c.c. of hot pure nitric acid, of sp. gr. 1·3, is now added, and the boiling continued for from fifteen to twenty minutes, to complete, as far as possible, the solution of the traces of silver still remaining in the gold which can be reduced to a limit of from 0·1 to 0·14 per cent. To prevent bumping of the concentrated acid during the second boiling, a piece of wood charcoal is introduced, or a charred pea or charred peppercorn.

After the second boiling, the acid is again poured off and the cornet washed twice with hot distilled water, the flask being filled completely from a glass vessel each time, whilst held in a slanting position.

After the washing is completed, the flask is once more filled with water and carefully inverted in a small unglazed annealing cup. The brittle dark brown gold cornet falls into the cup; the water is allowed to escape gradually from the flask by allowing it to overflow from the cup into a beaker. The water in the cup is then poured off as completely as possible, the slight remainder being absorbed by means of a strip of filter paper, care being taken that no gold is removed; the cup is dried for five minutes in front of the muffle, and then heated for a minute or two in the muffle to a bright red heat. The gold shrinks to about one-third of its former size, and becomes golden yellow in colour, lustrous, and coherent. The stamped number is distinctly visible. The cornet is then transferred to the pan of an assay balance and weighed to within 0·1 to 0·05 mg. The mean of the assays of "upper" and "lower" samples is taken as the true assay of the bar.

For simultaneously boiling a large number of samples, up to, say, 144, a very convenient form of platinum apparatus made by Messrs Johnson, Matthey & Co., is employed in the mint in London, and other places.[1] Parting cruets made of silica are also obtainable.

The results of assays of gold alloys are reported either decimally or by the "carat" system.[2] The decimal system is now being more generally adopted, but the older "carat" system is still largely used in England, as the workers and dealers in gold and silver alloys prefer this method of valuation. In these reports the alloys are referred to standard gold, 22 carat (916·6 per 1000), pure gold being 24 carat. The gold carat contains 4 grains, and the grain is subdivided into eight parts. In reporting how much gold in carats, grains, and eighths is present in an alloy above or below the legal "standard," the conventional terms "betterness" or "worseness" are used, the metal being reported as B^r when above standard and W^o when below; for example, a sample of 18-carat gold would be reported as 4 carats worse, the report reading:—

Gold Report.

	Carats.	Grains.
W^o	4	...

Standard, 22 carats.

In the reports of "parting" assays, in which both the gold and silver are returned in ounces of fine gold and silver in one pound troy, the abbreviations F.G. (fine gold) and F.S. (fine silver) are very frequently employed.

[1] For particulars of construction, see Jarman, *Trans. Inst. Min. and Met.*, 1905-6, **15**, 625.
[2] *Cf.* E. A. Smith, *J. Inst. Metals*, 1910, 3, 122.

Rose states that, with careful working, the error in the cornet assay does not exceed ±0·02 per 1000; this is confirmed by the very careful experiments of W. Witter.[1] The unavoidable loss of gold by absorption in the cupel and by volatilisation is almost exactly counterbalanced by the 1·2 to 1·4 parts per 1000 of silver remaining in the cornet.

In order to have a check on more material losses of gold, caused by an excessive temperature during cupellation, solution of gold, etc., check assays are generally made, using pure gold, pure copper, and the same amounts of silver and assay lead as are used in the assay itself, such check assays being cupelled alongside the assays proper. These checks generally show a surcharge of 0·1 to 0·4 per 1000, which has to be deducted from the assay values found.

Pure gold (assay gold) for this purpose was prepared by Roberts-Austen, at the London Mint, as follows:[2]—Cornets obtained from gold of a high degree of fineness were dissolved in aqua regia, excess of acid removed by evaporation, and platinum precipitated by adding potassium chloride and alcohol to the concentrated solution. The filtered gold solution, after diluting considerably with distilled water so that the strength was about 15 g. gold to 4·5 litres, was allowed to stand for about three weeks, to ensure precipitation of silver chloride; the clear liquid was then syphoned off, and the gold from 4·5 litres of solution precipitated in spongy condition, in the course of four days by the frequent addition of small quantities of pure oxalic acid, the solution being gently warmed during the precipitation. This was then repeatedly digested with hydrochloric acid, distilled water, and ammonia, and finally washed with distilled water, dried, and melted in a clay crucible, with acid potassium sulphate and borax. The purified gold was cast in a marble mould.

C. Whitehead[3] evaporates the gold chloride solution to dryness, dissolves the residue in water with the addition of a few cubic centimetres of hydrobromic acid, and dilutes the solution from 10 g. gold to 1·5 litre. The gold is precipitated from the absolutely clear syphoned solution by means of sulphur dioxide, again dissolved, and the above treatment repeated, the gold being finally washed, dried, and melted with borax and nitre.

Influence of Platinum Metals on Gold and Silver Assays.—Platinum and platinum metals are frequently contained in bullion, and their presence can frequently be detected by an examination of the beads obtained by cupellation. Valuable information is obtained by

[1] *Chem. Zeit.*, 1899, **23**, 522; *J. Soc. Chem. Ind.*, 1899, **18**, 768.
[2] *Fourth Annual Report of the London Mint*, 1873, p. 46.
[3] *Eng. and Min. J.*, 1899, **68**, 785; *J. Soc. Chem. Ind.*, 19, 1900, 148.

low power microscopical examination of bullion beads containing small quantities of the platinum metals.[1]

Platinum. The presence of small quantities of platinum in gold is indicated by the rough, crystalline appearance of the surface of the bead obtained by cupelling without addition of silver; larger quantities are indicated by the grey colour of the bead. With small quantities of platinum (up to 1·5 per cent.) the appearance of gold, silver and gold-silver beads under the low power objective of a microscope shows that there is a tendency for the boundaries of the crystals to become distorted and a banded or corrugated appearance is developed, which with increasing platinum content finally obscures the original structure of the metal or alloy and covers the whole of the bead. Platinum is separated from gold by cupelling the cornet obtained in the assay with eight times its weight of silver and lead, boiling with nitric acid, weighing the gold powder produced, repeating the alloying with silver, boiling, and so on, until the gold obtained is of constant weight[2] (*cf.* p. 155).

Priwoznik[3] states that platinum, to the extent of 2 per cent. of the weight of the gold, goes into solution in nitric acid along with the silver, the solution being colourless; traces of palladium, however, produce a pale yellow, and more palladium a brownish to reddish brown colour.

J. Spiller[4] states that the best solvent for platinum-silver is hot nitric acid of sp. gr. 1·42, which dissolves 0·75 to 1·25 per cent. of platinum along with the silver. Weak acid of sp. gr. 1·2 dissolves only 0·25 per cent. of platinum; the strongest acid is unsuitable, and brings about a separation of platinum black.

H. Carmichael[5] has shown that the solution of platinum is influenced by the proportion of platinum to gold, as well as by that of platinum to silver. For example, an alloy consisting of platinum 5 to 7 mg., gold 100 mg., silver 400 mg., on being boiled first in nitric acid of sp. gr. 1·171, followed by a second acid of sp. gr. 1·285, parted completely, all the platinum going into solution. Mass action seems to play a part in this process, for whereas the above alloy parted completely, an alloy consisting of platinum 14 mg., gold 200 mg., silver 800 mg., did not part, although an alloy of platinum 14 mg., gold 300 mg., silver 900 mg., parted completely.

[1] Bannister and Patchin, A simple method for the detection of platinum metals in cupellation beads, *Trans. Inst. Min. and Met.*, 1913-14, **23**, 163.

[2] *Cf.* C. Winkler, "Solubility of Platinum Silver in Nitric Acid," *Z. anal. Chem.* 1874, **13**, 369; *J. Chem. Soc.*, 1875, **28**, 428; see also, Oehmischen, *Berg u. Hütten. Zeit.*, 1901, **60**, 137; *J. Soc. Chem. Ind.*, 1901, **20**, 507.

[3] *Berg u. Hütten. Zeit.*, 1895, **44**, 325; *cf.* also, *Oesterr. Zeitschrift f. Berg u. Hütten.*, **47**, 356; *J. Chem. Soc. Abstr.*, 1900, **78**, 111.

[4] *Proc. Chem. Soc.*, 1897, **18**, 118; *Chem. Zeit.*, 1897, **21**, 477; *J. Soc. Chem. Ind.*, 1897, **16**, 539.

[5] *J. Soc. Chem. Ind.*, 1903, **22**, 1324.

From these results it will be seen that there should be about twenty times as much gold as platinum, and about three times as much silver as gold present, in order to part the gold completely from platinum and silver by means of nitric acid.

Palladium. Percy [1] stated that palladium gives a greenish stain and very crystalline beads, and according to Lodge,[2] when present in silver cupellation beads, palladium gives the surface a raised and embossed appearance and not a rough and pitted one like platinum. It is impossible to detect the presence of palladium up to 2 per cent. by the naked eye but under the low power objective of the microscope these small quantities give appearances similar to those given by platinum.

Minute quantities of palladium, however, even as little as 0·0002 g., impart a faint yellow colour to the parting acid.

According to Priwoznik, palladium cannot produce any considerable error in gold assays, as an alloy of 102 parts of palladium and 1250 parts of silver dissolves completely in strong nitric acid, forming a reddish brown solution.[3]

Iridium in gold produces rough, dark-spotted beads, on cupellation with silver and lead, from which rough, blistered, dark grey to black-spotted cornets are obtained, in which iridium can be detected in the blisters.[4] In quantities up 2 per cent., silver beads and gold parting beads show a stressed appearance under low power magnification.

In assay laboratories, *Iridium* and *Osmiridium* are usually separated from the gold by alloying with two or three times its weight of silver, and allowing the alloy to stand in the crucible for half to three-quarters of an hour in the molten state. The iridium and osmiridium sink to the bottom.

The presence of *Rhodium* even in traces may be detected by a crystallisation of the beads in which the facets of the crystals are distinctly visible. When over 0·03 per cent. is present, this is indicated by a bluish grey colour and much spitting. Iridium and rhodium remain almost entirely undissolved when the cornet is treated with aqua regia.

Ruthenium is indicated in cupellation beads by a black crystalline deposit firmly attached to the bottom edge of the bead.

Osmium volatilises as perosmic acid during cupellation.

Determination of Gold in Gold-Silver-Copper Alloys and in Auriferous Silver.—Two lots of 0·5 g. of the alloy are cupelled with sixteen times to thirty-two times the weight of assay lead, the percentage of base metal ascertained by loss, the bead alloyed, if necessary, by recupellation with silver, and parted by boiling with nitric acid, etc.

[1] *Metallurgy, Silver and Gold*, 1880, p. 271. [2] *Notes on Assaying*, 1904, p. 219.

[3] Cf. Schmidt, *Z. anorg. Chem.*, 1913, **80**, 335.

[4] Cf. Percy, *Metallurgy, Silver and Gold*, 1880, p. 272; Rose, *Metallurgy of Gold*, 1915, p. 506. Lodge, *Notes on Assaying*, 1904, p. 218.

According to C. Whitehead and T. Ulke,[1] in American mints and in the more important commercial laboratories in New York the noble metals in gold-silver alloys, rich in copper, are estimated as follows:—Ten grams of the sample is attacked by boiling with 100 c.c. of nitric acid (sp. gr. 1·2), the solution diluted to 300 c.c., and the gold collected on a filter; this is then dried, 2·5 g. of granulated lead added on the filter, which is then folded up and dipped into 5 g. of lead already melted on a scorifier; after limited scorification, the melt is poured and the button freed from slag and cupelled.

The hot filtrate from the gold is treated with a sufficiency of common salt and well agitated by means of compressed air. If over 0·06 per cent. of silver is present in the alloy, the silver chloride settles in half an hour. On account of the presence of traces of gold, the liquid is filtered through a double filter, and 2·5 g. of granulated lead is added on the filter. The whole is dried on a scorifier over the muffle, the paper then burnt by placing it in the muffle, 15 g. of lead and 0·5 of borax added, and the whole scorified. The button, which should weigh about 4 g., is cupelled, and the weighed bead parted.

R. van Liew[2] reduces the loss of gold experienced on dissolving copper containing noble metals in nitric acid, by lowering the working temperature. An assay ton of drillings is treated at ordinary temperature with 350 c.c. of water and 100 c.c. of nitric acid (sp. gr. 1·42); the solution occupies twenty-four hours. Air is then blown through the solution, 2 to 4 c.c. of normal salt solution added, and after standing for twelve hours, the precipitate is collected on a filter and washed. From 4 to 6 g. of assay lead is then added on the dried filter, the filter incinerated on a scorifier outside the muffle, and the scorification carried out with the addition of 3 or 4 g. of litharge and 3 or 4 g. of fused borax. This is followed by cupellation and parting.[3]

For the determination of gold in crude silver 10 g. is dissolved in a long-necked flask in 80 to 100 c.c. of nitric acid (sp. gr. 1·2), the silver solution is decanted into a litre flask, and the residual gold again boiled with nitric acid, sp. gr. 1·3; the solution is again decanted, the residue washed repeatedly with hot distilled water, all the wash water united in the litre flask, and the gold collected in an annealing cup, dried, ignited, and weighed.

The silver solution is cooled to the ordinary temperature, and diluted to exactly 1 litre; 100 c.c. (corresponding to 1 g. of the sample) is then titrated with ammonium thiocyanate (*cf.* Vol. I., p. 643, and Silver, this Vol., p. 122).

[1] *Eng. and Min. J.*, 1898, **65** [7], 189; *J. Soc. Chem. Ind.*, 1898, **17**, 379; *Chem. Zeit. Rep.*, 1898, **22**, 69.

[2] *Eng. and Min. J.*, 1900, **69**, 469, 498; *Chem. Zeit. Rep.*, 1900, **24**, 147.

[3] Cf. also Offerhaus, *Metall. u. Erz*, 1917, 276.

Gold alloys, containing tin and zinc, are assayed by scorification with twenty times their weight of assay lead and a quarter their weight of borax; the lead button obtained is cupelled with the necessary silver and the resulting bead is parted.

Assay Methods without Cupellation.

Inquartation with Silver.—The following modification of the ordinary assay is due to Bock.[1] Cupellation, with its attendant loss of gold, is avoided by alloying the rich bullion with the requisite amount of silver in a small graphite crucible, flattening out the button, re-melting, and then making the cornet and boiling twice with nitric acid in the usual way; the minute remainder of silver is then removed electrolytically, by subjecting the cornet to a current not exceeding 1 ampère per square metre of cathode surface for ten minutes in a platinum crucible, the electrolyte consisting of very weak nitric acid (one volume nitric acid of sp. gr. 1·2 to five volumes of water).

An examination of this method by Witter and Bock showed the results to be excellent. It is unsuitable for brittle gold, which, even when alloyed with silver, cannot be either beaten out or rolled, but it is well suited for malleable gold and malleable gold-silver-copper alloys.

Inquartation with Cadmium.—This method, due to Balling,[2] is carried out without cupellation in a muffle, and both silver and gold can be determined in the same sample.

According to Kraus,[3] satisfactory results are obtained by the following modification:—About 3 g. of potassium cyanide is melted in a small porcelain crucible, 250 mg. of the alloy (gold bullion) added, and then two and a half times its weight of cadmium; after melting down, the whole is shaken round, whereupon a silver-white mobile alloy is produced. After cooling, the potassium cyanide is removed with water, the button (or, if two samples are treated, both buttons) transferred to a parting flask and treated with nitric acid (sp. gr. 1·2), a charred pea introduced, and the whole heated for some time; in the assay of fine gold, the boiling occupies one hour. The solution is decanted, and the residue washed once with hot water, after which it is boiled for ten minutes with nitric acid of sp. gr. 1·3, the solution poured off, the residue washed with hot water, and boiled for five minutes with water, which is then poured off; the flask is then filled with water, the gold transferred to a small porcelain crucible, dried, and ignited, and the beads weighed, either separately or together.

If the decanted acid and washings are collected, the silver can be

[1] *Chem. Zeit.*, 1897, **21**, 973; 1898, **22**, 358; 1899, **23**, 49; *J. Soc. Chem. Ind.*, 1898, **17**, 695.
[2] *Oesterr. Zeitschrift*, 1879, p. 597; 1881, No. 3.
[3] *Dingl. polyt. J.*, 1880, **236**, 323; *Berg. u. Hütten. Zeit.*, 1880, **39**, 219; *J. Chem. Soc. Abstr.*, 1880, **38**, 679.

determined as silver chloride, after evaporation, or it can be estimated volumetrically by the Volhard method (p. 122).

The cadmium alloy is brittle and cannot be flattened; consequently, prolonged boiling of the bead with nitric acid is necessary; the final boiling with water must also be very thorough, in order to remove the last traces of cadmium nitrate.

Determination of Gold in various Alloys.

Alloys rich in copper may be assayed by scorification and cupellation, or by the combined wet and dry method (*cf.* p. 114). If the copper is small in amount, the alloy may be cupelled, according to Kerl, with addition of silver; the silver must be about three times the reputed gold content, otherwise the gold bead will contain copper.

Lead- and *Bismuth-gold alloys* are cupelled direct, but poor alloys may be first concentrated by a preliminary scorification.

Auriferous antimony may be assayed as follows:[1]—Thirty grams of powdered antimony is mixed with 60 g. of litharge, 12 g. of nitre, and 12 g. of sodium carbonate, and melted in a crucible for a quarter of an hour at a low red heat in a wind-furnace; the melt is poured into a mould, and the button cupelled. The slag from the melt is run down with 30 g. of litharge and 1·2 g. of charcoal; the button from this is also cupelled.

For the assay of alloys of gold with platinum and the platinum metals, *cf.* Platinum, pp. 154, 157.

Electrolytic Determination of Gold.—Gold is seldom determined electrolytically,[2] although the electrolytic determination of gold in cyanide solutions is used to a considerable extent in South Africa.

Imitation Gold Alloys.—According to Weber, these alloys show a black coloration on the surface when treated with one drop of a concentrated solution of cupric chloride; the surface should first be cleaned with alcohol and ether. Gold alloys, and even thinly-plated goods, do not react thus. Solutions of silver nitrate and gold chloride have a similar action. The streak produced on the touchstone by imitation alloys disappears on treatment with strong nitric acid.

Very thin plating is detectable, according to R. Finkener, by taking a piece of material weighing 0·1 to 1·5 g., washing with alcohol and ether, and then treating it in a beaker with 0·5 to 10 c.c. of pure nitric acid (sp. gr. 1·3). Tiny gold leaflets are soon observable on the bottom of the beaker and also floating on the surface of the liquid.

If wash-gilded material is similarly treated, the more coherent gold particles appear rough on the under side and are somewhat darker in colour.

[1] E. A. Smith, *J. Soc. Chem. Ind.*, 1893, **12**, 316; *Chem. News*, 1893, **67**, 195.

[2] Cf. *Quantitative Chemical Analysis by Electrolysis*, A. Classen, 1919.

PLATINUM

Platinum ores, the metal itself, and the platinum metals and their alloys, are seldom assayed in commercial laboratories. Their content and value are almost exclusively determined in the laboratories of the dealers in London, Hanau, Frankfort-on-Main, Paris, and New York, where worn-out sulphuric acid pans and old platinum laboratory utensils are also sent to be re-worked.

The quantitative separation of the individual platinum metals is a matter of considerable difficulty.

The raw materials for the manufacture of platinum and the platinum metals are :—

Native Platinum, obtained by washing alluvial deposits and also from norite deposits. The metal is usually accompanied by gold, osmiridium, and many specifically heavy minerals, such as chrome iron ore, titanic iron ore, magnetite, zircon, spinelle, etc.

Sperrylite, $PtAs_2$, containing a little rhodium and antimony, found only in Canada, accompanying nickel ores.

The *Platinum Metals*, obtained in the parting of gold-silver alloys, in the electrolytic refining or parting of gold and in the residues from the Mond nickel process.

According to Kerl,[1] native platinum (washed platinum) contains, on the average, from 80 to 86 per cent. of platinum, 1 to 8 per cent. of iridium, 1 to 8 per cent. of osmiridium, 0·25 to 2 per cent. of palladium, 0·4 to 3 per cent. of rhodium and ruthenium, 5 to 13 per cent. of iron and copper, and 1 to 4 per cent. of sand. In the ore from the Urals, the content of iridium, rhodium, and palladium together is usually 4 to 5 per cent., and the residue insoluble in aqua regia and consisting chiefly of osmiridium, is about 8 per cent.

ASSAY METHODS FOR ORES[2]

Originally the ores were assayed and worked in the wet way; a combination of wet and dry processes is now employed.

Deville and Debray's Dry Method for Platinum Sand.[3]

1. *Gangue* (Quartz, Chromite, Titanic Iron Ore, etc.). Several samples, of 2 g. each, are fused with 7 to 10 g. of fine silver, under a layer of 10 g. of borax, in small, glazed, clay crucibles. The temperature must be considerably above the melting point of silver. The borax is

[1] *Muspratt-Stohmann's Handbuch der technischen Chemie*, 4th edition, vol. vii. (1898), p. 260.

[2] Cf. *ibid.*

[3] *Ann. Chim. Phys.*, 1859 (iii.), **56**, 385; *Berg. u. Hütten. Zeit.*, 1860, **19**, 256; *Z. anal. Chem.*, 1913, **52**, 660.

well stirred with the stem of a clay pipe and the whole is allowed to cool, when the borax and other material are separated from the metallic button, if necessary, by warming with dilute sulphuric acid and hydrofluoric acid. The difference in weight of the button and that of the sample plus silver gives the weight of gangue.

2. *Gold.* An average sample, weighing 10 g., is boiled continuously for several hours with water, frequent small additions of mercury being made from time to time. The whole of the mercury is run through a pierced filter paper, the mercury distilled off in a small retort, and the residue of spongy gold strongly heated and weighed. The results are tolerably accurate, but generally too low by a negligible amount.

Instead of boiling with mercury, the ore may be made into a thick pulp with water, and then ground with mercury for some hours in an iron mortar. The residue is then washed from the mercury and the latter treated as above (Bannister).

3. *Platinum.* Fifty grams of ore is fused with 75 g. of assay lead and 50 g. of pure galena, in a fire-clay crucible, under a layer of 15 g. of borax, and mixed with the stem of a clay pipe, until all the beads are alloyed with the lead; the temperature is gradually raised to the melting point of silver, then 50 g. of litharge is added, and the temperature still further raised for a short time. The platinum metals (except osmiridium) alloy with the lead, and osmiridium collects at the bottom. The sulphides of copper and iron, produced by the action of the galena, are oxidised by the litharge, and the oxide is slagged. When evolution of sulphur dioxide has ceased, the crucible is allowed to cool, and the button, which weighs about 200 g., cleaned; the lower portion, to the extent of about one-tenth of the button, is then sawn off and weighed. The main portion of the hard alloy, together with the grains from the sawing, is weighed and powdered, and one-ninth of it is cupelled.

A considerable amount of lead, at least 6 or 7 per cent., remains with the platinum; according to Deville and Debray's process, it is removed by an oxidising fusion in a small lime furnace, using an oxyhydrogen flame with excess of oxygen.

To avoid this treatment, the lead-platinum alloy can be cupelled at a high temperature with five to six times its weight of silver (accurately weighed), and, in addition, assay lead. The increase in weight of the silver gives the platinum content of one-ninth of the total, so that nine times this value gives the amount in the whole upper portion of the lead-platinum alloy.

The silver-platinum alloy, after being rolled out quite thin, can be parted by continued boiling with concentrated sulphuric acid.

The lower tenth of the large lead-platinum button, which was sawn

off, is broken down and warmed for some time with ten times its weight of nitric acid (sp. gr. 1·2) and an equal quantity of water, in order to dissolve out the lead ; the residue, consisting of osmiridium prills and leaflets and platinum black, is thoroughly washed by decantation, first with hot water containing nitric acid, and finally with hot water, then dried and weighed. The platinum is then dissolved out with hot aqua regia and the unchanged osmiridium washed, dried, and weighed.

The percentage of platinum with platinum metals, and also that of osmiridium, is thus ascertained.

The pure platinum contained in the ore is from 4 to 5 per cent. less than the amount found, since the platinum in Russian ore is alloyed, fairly evenly, with 4 to 5 per cent. of the other platinum metals ; the percentage of osmiridium, however, varies considerably.

The following is a very suitable method for the examination of platinum-bearing sands, etc. The crushed material is fluxed in a pot with red lead, etc., in order to obtain a lead button, as described under the assay of silver and gold ores. The lead button is cupelled, and the resulting bead rolled out and boiled in dilute sulphuric acid, the acid being allowed to get stronger gradually. The residue is washed, boiled in nitric acid, and again washed. The two resulting solutions contain the silver. The residue is then dissolved in aqua regia. Osmiridium remains, together with a trace of silver chloride and lead sulphate ; the silver chloride may be dissolved in ammonia, and the lead sulphate in ammonium acetate solution. The osmiridium is then washed, weighed, and further examined, if necessary. The aqua regia solution contains platinum and gold ; the platinum may be precipitated by ammonium chloride, and gold by ferrous sulphate (Bannister).

Wet Assay for Ores.[1]

In the former St Petersburg Mint 5 to 10 g. of gold-free ore was repeatedly digested for eight or ten hours in a porcelain dish with aqua regia (one volume nitric acid of sp. gr. 1·34 to three volumes hydrochloric acid), until a yellow solution was no longer obtainable. A concentrated solution of ammonium chloride was added to the solution, which contained platinum, iridium, palladium, rhodium, etc., and the precipitate, coloured red by iridium, was transferred to a filter, washed with alcohol, dried, and gently ignited. On prolonged digestion of this residue with considerably diluted aqua regia (1 : 4 or 1 : 5) at 40°, only platinum went into solution. From the difference between the weight of the platinum black containing iridium and that of the iridium obtained, the amount of pure platinum was ascertained.

[1] For the determination of platinum in copper ores (Wyoming) *cf.* Dart, *Chem. and Met. Eng.*, 1912, 10, 219.

The following method, due to Hess,[1] can be recommended. The ore is fused with four times its weight of zinc, and the finely powdered alloy treated first with weak, then with strong sulphuric acid, whereby the zinc is dissolved; the copper and lead are then dissolved out with nitric acid, and the washed residue treated with aqua regia. The separation of platinum, etc., is effected as above.

Miller[2] scorifies platinum ores with assay lead, then dissolves out the lead by warming the button with dilute nitric acid of sp. gr. 1·05, oxidises the residue by roasting, and boils again for ten minutes with nitric acid. The washed and dried residue is weighed as crude platinum. If it contains gold, it is treated with weak aqua regia (1 : 5), the filtered platinum-gold solution evaporated to dryness, very weak hydrochloric acid added, and the gold precipitated with oxalic acid, filtered off, washed, dried, and cupelled with a little lead. The difference between the weight of crude platinum and of the residue from the treatment with aqua regia plus the weight of gold, gives the weight of platinum which has gone into solution.

The iridium is dissolved from the residue left on treatment with aqua regia, by heating with strong aqua regia; the final residue is only osmiridium.

The solutions obtained from gold-bearing ores are evaporated to dryness on the water-bath with addition of ammonium chloride, the residue is extracted with absolute alcohol, to remove the ammonium aurichloride and the gold precipitated from the solution with ferrous sulphate, after removal of the alcohol and acidifying with hydrochloric acid.

The residue from the treatment with alcohol is dried, the ammonium chloride volatilised, the residue ignited, and the platinum dissolved out with weak aqua regia, in accordance with the method given above.

For the *Electrolytic Separation of Platinum*, *cf.* Classen, *Chemical Analysis by means of Electrolysis*, English translation, 1919, p. 141.

Platinum Alloys

1. Platinum, Gold, and Copper.

Copper is removed by cupelling with eight to thirty times the weight of lead, at a high temperature; the bead is then flattened, treated with aqua regia, the platinum precipitated as ammonium platinichloride by evaporation with ammonium chloride, and the gold precipitated from the hydrochloric acid filtrate with ferrous sulphate.

[1] *Dingl. polyt. J.*, 1854, **133**, 270.

[2] *School of Mines Quarterly* (Columbia University, New York), **17**, 26; *Berg u. Hütten. Zeit.*, 1896, **55**, 235; *J. Soc. Chem. Ind.*, 1896, **15**, 379.

2. Platinum, Silver, and Copper.

The alloy is cupelled with eight to thirty times its weight of lead and sufficient silver to give, in the resulting alloy, five parts of silver to one of platinum.[1] The approximate platinum content must be ascertained by a preliminary assay. The flattened bead is boiled for a quarter of an hour with concentrated sulphuric acid, and the resulting platinum powder similarly treated with dilute sulphuric acid, and finally with water. The residue is then transferred to a small crucible, in the same way as the gold powder in the gold assay. Any retained silver is determined by dissolving in aqua regia, evaporating, and filtering from platiniferous silver chloride, then dissolving the silver chloride in ammonia and reprecipitating it by acidifying with nitric acid.

3. Platinum, Silver, and Gold (with Copper and Osmiridium).

Two hundred mg. of the alloy is cupelled with eight to thirty times as much lead, sufficient silver being added to ensure a ratio of three parts of silver to one of gold in the resulting alloy; copper is determined by difference. The alloy is then flattened and rolled, with repeated annealing, the cornet boiled first with concentrated sulphuric acid, then with dilute sulphuric acid, and finally with water, after which it is dried, ignited, and weighed. The loss, less the amount of added silver, represents the silver in the 200 mg. of original alloy taken for the assay. The cornet is then cupelled with an excess of silver (at least twelve times the weight of the presumed, or approximately determined, platinum content) and assay lead, a fresh cornet made, and boiled first with nitric acid of sp. gr. 1·16, then with somewhat stronger acid of sp. gr. 1·26; the platinum and silver go into solution.[2]

On treatment of the residue, consisting of gold and osmiridium, with aqua regia, only gold goes into solution, and this is precipitated in the usual way.

4. Platinum and Iridium.

Alloys of platinum and iridium are largely used in the construction of thermo-electric pyrometers and may be assayed by cupellation and parting or by alloying with lead and parting.[3] In the cupellation method, 0·25 g. of the alloy and 1·5 g. of pure silver are cupelled with 10 g. of assay lead at a high temperature. The button is rolled into a cornet and parted with concentrated sulphuric acid, being boiled in two successive portions of 40 c.c. The residue is boiled twice with dilute aqua regia (HCl : 4, HNO_3 : 1, H_2O : 10 parts by volume) to

[1] Riemsdijk, *Berg u. Hütten. Zeit.*, 1886, **45**, 213.

[2] With regard to the solubility of platinum-silver alloys in nitric acid, *cf.* Gold Inquartation, p. 146.

[3] Bannister and Du Vergier, *Analyst*, 1914, **39**, 340.

dissolve the platinum, then washed with water, dilute ammonia, and water in succession, ignited at a high temperature and weighed as iridium.

In the lead method, 0·5 g. of the alloy is heated for one hour with 5 g. of assay lead in a carbon crucible contained in a clay crucible, placed in a wind furnace. The lead button obtained is digested with two successive portions of 50 c.c. of dilute nitric acid (1 : 10), the residue being treated with dilute aqua regia as in the cupellation method given above. The platinum may be determined in both methods by precipitation with pure zinc and subsequent ignition of the metal in hydrogen.

5. Analysis of Metallic Platinum.[1]

Commercial or Impure Platinum. Ten g. of the metal is dissolved in aqua regia and the solution evaporated with 6 g. of sodium chloride. The residue is evaporated several times with water, then heated for one hour at 120°, treated with about 100 c.c. of water and the solution filtered. The small residue may contain silicates, iron salts, silver chloride, etc., and is analysed separately. The solution is diluted to 500 c.c., made faintly alkaline with 0·8 g. of sodium bicarbonate, heated to boiling, cooled, and again heated with a solution of 0·8 g. of sodium bicarbonate in 20 c.c. of saturated bromine water; the solution should remain faintly alkaline.

When a test portion of the yellow solution no longer gives a dark coloration with the hypobromite solution, the whole is filtered (after the addition of alcohol, if necessary, to coagulate the precipitate) and the black precipitate is washed with water, the filtrate being heated with alcohol and filtered through a separate filter. The solution contains practically the whole of the platinum as platinum sodium chloride, and the precipitate consists mainly of the oxides of the foreign metals present, together with some platinum. The precipitate is dissolved in hydrochloric acid and saturated with ammonium chloride; the precipitate obtained is filtered after standing one hour and is washed with ammonium chloride solution. This precipitate contains a little platinum with palladium, some iridium and possibly ruthenium. It is heated in a current of hydrogen, ultimately to incandescence, and the reduced metal treated with dilute aqua regia which dissolves platinum and palladium.

The insoluble residue consists of iridium and may contain ruthenium. After weighing, it is ignited with 0·5 g. of sodium nitrate in a gold or silver spoon. Ruthenium, if present, will dissolve in the melt forming a yellow mass, while iridium remains as a blue residue which is separated and weighed. The aqua regia solution of platinum

[1] Mylius and Nazzucchelli, *Z. anorg. Chem.*, 1914, **89**, 1; *J. Soc. Chem. Ind.*, 1915, **34**, 84.

and palladium is treated with ammonium chloride for the precipitation of platinum, and the palladium is precipitated from the filtrate by means of mercuric cyanide. The filtrate from the first precipitation of platinum, iridium, etc., is evaporated to dryness with 3 c.c. of dilute nitric acid and the residue treated with dilute nitric acid so as to obtain a solution nearly saturated with ammonium chloride; if there is any residue it is filtered off, washed with a nitric acid solution of ammonium chloride, and added to the main palladium-iridium-ruthenium precipitate for treatment as above. The filtrate obtained is evaporated with hydrochloric acid, the residue dissolved in 5 c.c. of water with the addition of one drop of dilute hydrochloric acid and then rapidly saturated with hydrogen sulphide at about 18°. The black precipitate of copper and gold sulphides is filtered off and washed, and the gold and copper are separated.

The filtrate from the gold-copper precipitate is warmed and treated with hydrogen sulphide for half an hour. The excess of hydrogen sulphide is boiled off and the brown precipitate, which consists of rhodium sulphide, is filtered off. This is ignited in hydrogen and weighed. The solution from the rhodium may contain iron, zinc, nickel and cobalt, which are separated by a suitable method.

Nominally Pure Platinum. Fifty g. of the metal is converted into the sodium platinum chloride as described above, which is crystallised several times from a one per cent. solution of sodium carbonate. The mother liquors, together with the solution obtained by treating the small quantity of insoluble matter left from the first operation, are evaporated first with aqua regia and then with hydrochloric acid and the residue heated to 150°, taken up with water and filtered. This solution may be analysed as described under impure platinum.

6. Dental Alloys.

A detailed procedure for the analysis of dental gold alloys which usually contain gold, platinum, palladium, iridium, rhodium and copper, is given by W. H. Swanger.[1] All the constituents of a dental gold alloy are usually determined in the same sample.

A 2 g. sample is dissolved in 25 c.c. of dilute aqua regia, the silver chloride formed being broken up from time to time with a glass rod until the alloy is completely decomposed, after which the solution is evaporated to small bulk, 200 c.c. of water is added and the whole digested on the steam bath for one hour.

(a) *Silver and Iridium.* The silver chloride is filtered off, and after washing well with water is dissolved by pouring on hot dilute

[1] "Analysis of Dental Gold Alloys," *Scientific Papers of the Bureau of Standards*, No. 532, Washington, U.S.A., 1926.

ammonium hydroxide. Iridium, if present, is left as a black metallic residue on the paper, and after washing several times with hot 1 per cent. ammonium hydroxide, both are transferred to a beaker and digested for thirty minutes on a steam bath with 15 to 25 c.c. of dilute ammonium hydroxide. The residue is filtered off on a small paper, washed well with hot 1 per cent. ammonium hydroxide, transferred with the paper to a porcelain crucible, dried and ignited in air. After the combustion of the carbon is complete, the residue is ignited in hydrogen (Rose crucible method), allowed to cool in an atmosphere of the same gas and then weighed as metallic iridium. This method is satisfactory when not more than 0·2 or 0·3 per cent. of iridium is present in the sample, and is suited to dental alloys, which do not usually contain over 0·2 per cent.

Silver chloride is reprecipitated from the ammoniacal filtrates and washings by acidifying with nitric acid, after which it is filtered off on a Gooch crucible, washed well with water, dried at 110° and weighed.

Platinum and palladium contained in the filtrate from the reprecipitation of the silver chloride are recovered and added to the main solution of the sample obtained from breaking down the alloy with dilute aqua regia. The procedure is as follows: The filtrate from the reprecipitation is evaporated to dryness and ammonium nitrate destroyed by cautiously adding hydrochloric acid. The residue is evaporated to a small volume, transferred to a porcelain crucible, evaporated to dryness and the residue fused for thirty minutes with 10 g. sodium pyrosulphate. After cooling, the melt is dissolved in hot water, heated to incipient boiling, and at this temperature sulphuretted hydrogen gas is passed for half an hour. The platinum and palladium sulphides are filtered off, washed, ignited to metal, dissolved in a few c.c. of dilute aqua regia and the solution, after filtering off any silica, added to the main solution of the sample.

(b) *Gold.* Gold is now determined in the combined solution in the following manner:—The liquid is evaporated to dryness on a steam bath, the residue taken up with a little water, 10 c.c. hydrochloric acid added and the liquid diluted to about 200 c.c. 50 c.c. of a saturated solution of sulphur dioxide is added, the solution digested on the steam bath for one hour, a further 20 c.c. of the solution added and set aside to cool. The supernatant liquid, which should smell strongly of sulphur dioxide, is decanted off, through a pulp filter, and the precipitated gold washed by decantation with a hot 1 per cent. hydrochloric acid solution, passing the washings through the filter. The latter is then washed thoroughly and returned together with the small amount of gold caught on it to the beaker.

The precipitated gold, which carries appreciable amounts of platinum and palladium, is dissolved in 20 c.c. of dilute aqua regia, and after filtering and washing with 1 per cent. hydrochloric acid, the filtrate is evaporated to dryness on a steam bath. To ensure the complete removal of nitric acid 3 c.c. of hydrochloric acid is added and the evaporation repeated two or three times.

The final residue is taken up with 5 c.c. of hydrochloric acid, about 10 drops of sulphuric acid and 150 c.c. of water, and the gold is precipitated by adding 50 c.c. of a saturated solution of oxalic acid and boiling for fifteen minutes. The gold which is precipitated as a bright metallic sponge is filtered off, washed thoroughly, ignited and weighed.

(c) *Palladium.* In order to recover the platinum and palladium precipitated with the gold by sulphur dioxide, the above filtrate is evaporated to dryness, 5 c.c. of sulphuric acid added and the mixture evaporated until only a little acid remains. The residue is treated with 10 c.c. of dilute aqua regia to dissolve the metals, the solution is filtered off and added to the filtrate from the first precipitation of the gold.

The combined solution is evaporated to dryness, the residue dissolved in 10 c.c. of dilute aqua regia, the resulting solution is diluted to about 250 c.c., cooled to 15°, after which sufficient dimethylglyoxime (1 per cent. solution in alcohol) to precipitate the palladium is added; 1 g. of palladium is precipitated by 2·2 g. of the reagent.

The solution, which must not be heated, is allowed to stand one hour, after which the precipitate is filtered off on a paper of suitable size and washed well with hot water. Paper and contents are returned to the beaker, treated with 25 c.c. of dilute aqua regia and heated on a steam bath until the precipitate is dissolved. The paper pulp is filtered off, washed with hot water and ignited, any metallic residue therefrom being dissolved in a few c.c. of dilute aqua regia and added to the main palladium solution. About 250 c.c. of water is now added, the palladium precipitated as before, collected on a Gooch crucible washed with hot water, dried at 110° and weighed. Precipitate $\times$ 0·3167 = Pd.

(d) *Copper.* The filtrates from the palladium precipitation are combined and evaporated to dryness. The residue is digested on the steam bath with 5 c.c. of nitric acid, and the solution is again taken to dryness, after which the residue is treated with 10 c.c. of hydrochloric acid and enough water to dissolve the salts present.

If copper is present it is determined, after reduction by a saturated solution of sulphur dioxide in water, by the thiocyanate method (p. 179).

(e) *Rhodium and Platinum.* The filtrate from the copper thiocyanate is evaporated to dryness, the residue is digested with 5 to 10 c.c. of nitric acid to destroy the excess of thiocyanate, and after

evaporating to dryness a second time 5 to 10 c.c. of sulphuric acid is added and the mixture evaporated to "fumes." After cooling, 20 c.c. of dilute hydrochloric acid is added, the solution is diluted with 100 c.c. of water and filtered. The residue is leached with dilute aqua regia to dissolve any trace of platinum retained by it, the solution is evaporated to expel nitric acid and subsequently taken up with hydrochloric acid and added to the main solution, which contains platinum, together with rhodium, nickel, zinc, and manganese, if present. A fairly rapid stream of sulphuretted hydrogen is passed through this solution for at least thirty minutes, while it is heated to incipient boiling, the precipitate is filtered off, washed thoroughly with hot 1 per cent. hydrochloric acid, ignited over the full heat of a Bunsen burner and the platinum-rhodium sponge weighed.

Separation of the rhodium from the platinum is made by Wichers' method[1] in the following manner:—The sponge is dissolved in 15 to 20 c.c. of aqua regia, the solution evaporated nearly to dryness and then diluted to 200 c.c. The free acid is neutralised with sodium hydroxide solution, using cresol red as indicator, then suspended barium carbonate (freshly prepared by mixing 5 c.c. of a solution containing 90 g. of barium chloride per litre and 5 c.c. of a solution containing 36 g. of anhydrous sodium carbonate per litre) is added, the solution rapidly heated to boiling, and after boiling two minutes the residue is filtered off and washed well with hot 2 per cent. sodium chloride solution. The residue is returned with the paper to the beaker, digested with dilute hydrochloric acid (1 : 4), the solution is then freed from paper pulp by filtration, again neutralised, and treated with barium carbonate exactly as before; it may be necessary to repeat this operation again to ensure complete removal of platinum. The rhodium hydroxide-barium carbonate mixture is subsequently dissolved in dilute hydrochloric acid and the rhodium is precipitated by the use of sulphuretted hydrogen. The rhodium sulphide is filtered off at once, washed with a hot 1 per cent. ammonium chloride solution, ignited in a crucible and finally reduced and cooled in an atmosphere of hydrogen, using a Rose lid and delivery tube. The residue is weighed as metallic rhodium and the weight thus obtained is subtracted from the weight of mixed sponge to obtain the weight of platinum.

(f) *Zinc, Nickel, Manganese.* The filtrate from the original precipitation of platinum and rhodium as sulphides is treated by one of the methods in general use for the determination of these metals.

Recovery of Platinum from Platinum Residues obtained in potassium estimations; *cf.* p. 400.

[1] *J. Amer. Chem. Soc.*, 1924, 46, 1818.

MERCURY

The most important ore of mercury is *Cinnabar*, which, in its purest form, contains 86·21 per cent. of mercury; tiny drops of metallic mercury are occasionally found in it.

Idrialite is a peculiar variety of cinnabar from Idria; it is a mixture of cinnabar with idrialine (a hydrocarbon which is present in idrialite to the extent of as much as 75 per cent.), iron pyrites, clay, and gypsum. Hepatic cinnabar and the spathic iron ore of Idria contain cinnabar, idrialine, bitumen, and other carbonaceous substances, in very varying amounts.

Other mercury ores are *Calomel*, *Mercury selenide*, and the *Silver amalgams*, containing varying percentages of mercury, but they are not found in large quantities and do not call for commercial examination. As much as 17 per cent. of mercury occurs in some Hungarian and Tyrolese fahl ores.

The most frequently employed method of assaying mercury ores is the rapid gold amalgamation assay, due to Eschka; it gives satisfactory results. Distillation tests, in which the mercury is collected as such, are practically only used as works' tests. Purely analytical wet methods are very seldom used, though electrolytic methods are occasionally employed.

Distillation Test for Mercury.

Average samples, up to 2 kg. in weight, are mixed with from one-half to an equal weight of black flux, and heated to a bright red heat in earthenware or iron retorts or pipes, and the mercury is condensed by water-cooling.

H. Rose's[1] distillation method, carried out on a smaller scale, gives very good results. The mercury compounds (cinnabar, calomel, corrosive sublimate, sulphate, etc.) are decomposed with calcium oxide at a moderate temperature in a hard glass combustion tube; the mercury vapour is driven out of the tube by means of carbon dioxide, and condensed by cooling. The method is carried out as follows:—

A layer of roughly powdered magnesite (which is better than either chalk or sodium bicarbonate), 25 to 50 mm. in length, is introduced into a combustion tube closed at one end and having a length of 30 to 45 cm., with a diameter of 10 to 15 mm.; a mixture of ore and burnt lime, and then a layer of lime and a loose plug of asbestos, are placed in front of the magnesite. The end of the tube is drawn out and bent downwards at an obtuse angle. By carefully tapping the tube, while it

[1] Rose-Finkener, *Handbuch d. analytischen Chemie*, vol. ii., pp. 187 *et seq.*

is held in a horizontal position, a channel is formed for the subsequent escape of the carbon dioxide. The tube is placed in a furnace, which slopes slightly, and is heated, first at the end where the free lime is contained, until it attains a red heat at this section; the mixture itself is then heated, and finally the magnesite. The drawn-out end of the tube dips under water contained in a small flask, in which almost all the mercury is collected; the end of the tube is cut off, and the drops of mercury remaining therein are washed out and added to the bulk in the flask. An open combustion tube is sometimes used, coal gas being passed through during the distillation. The collected mercury is transferred to a tared porcelain crucible, the water poured off as completely as possible, and the remainder removed by absorption with filter paper, after which the crucible is placed for a short time in an air-bath (or preferably for several hours in a desiccator over sulphuric acid), dried, and weighed.

This method must be used if the material under investigation contains notable quantities of mercury salts (chlorides, sulphates), which volatilise partially undecomposed, if the Eschka method is employed.

The Eschka Gold Amalgamation Assay.

This method has been especially worked out in Idria. A Meissen porcelain crucible is used in the assay, about 45 mm. deep, upper diameter 48 mm., lower 22 mm., and of 50 c.c. capacity; the edge must be true, and it must be provided with a well-fitting lid of gold, weighing about 10 g., having a depth of from 6 to 8 mm., and of the shape shown in Fig. 44.

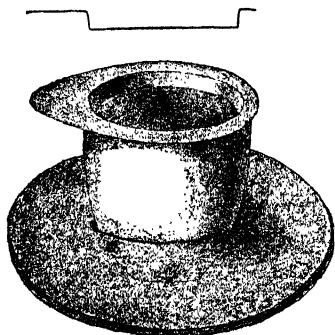



FIG. 44.

According to C. Winkler, a lid of pure silver may be used, but a very small mercury deposit cannot then be detected with certainty.

Holloway used a flat silver plate kept cool by means of a stream of cold water running through a metal box placed on the top of the plate.

The amount of ore to be taken for the assay depends on the richness in mercury: with ores containing up to 1 per cent., 10 g. should be taken; with 1·5 to 10 per cent. of mercury, 5 g.; with very rich ores, 0·5 to 2 g. suffice. The approximate value is ascertained by a preliminary assay, using 1 g. of material. The ore is mixed in the crucible with half its weight of iron filings, which must be absolutely free from oily impurities, a 5- to 10-mm. layer of iron filings put on the top, and the weighed gold

or silver lid placed in position and carefully pressed tight on to the crucible edge by means of a smooth metal plate; the lid is filled with distilled water, and the crucible bottom is then heated for ten to fifteen minutes by means of a gas or spirit flame. The crucible should be placed in an asbestos ring in order to protect the upper part of the crucible and the lid from unnecessary heating. After cooling, the lid is removed, the water poured away, the lid washed on both sides with alcohol, dried on a watch-glass over a hot water-bath for two or three minutes and weighed after a quarter of an hour. The mercury is subsequently removed by heating the lid carefully over a small Bunsen flame, in a draught cupboard.

If too much ore is taken, the large quantity of mercury deposited on the lid requires very careful washing, and the lid is also affected by the excessive amount of mercury, and after volatilisation of the deposit, the surface remains rough and no longer fits accurately on the crucible; a preliminary assay should therefore be made, if the mercury content of the ore is quite unknown.

Small losses of mercury, during the progress of the assay, are unavoidable. Balling states that in Idria the following corrections are added:—

Ore Value.	Correction.
Hg per cent.	Per cent.
Up to 0·4	0·04
0·4 ,, 0·7	0·06
0·7 ,, 1	0·08
1 ,, 3	0·15
3 ,, 5	0·20
5 ,, 10	0·25
10 ,, 20	0·35
20 ,, 30	0·45
30 and over	0·50

Bituminous ores, when decomposed by means of iron only, give tarry distillation products, which collect with the mercury and cannot be removed by mere washing. According to Eschka, if red lead is added complete combustion of the bitumen is effected, but there is, at the same time, a slight volatilisation of lead, and also a superficial oxidation of the mercury.

To overcome this difficulty, the following modification of the Eschka process is employed in Idria:[1]—Rich and medium ores are mixed with well-ignited hammer-scale, which has been passed through a fine sieve; above this is placed a layer of hammer-scale, and, on top of all, oxide of zinc. Poorer ores are mixed with ignited barium carbonate, and the mixture is covered with hammer-scale and zinc oxide.

[1] Kroupa, *Berg u. Hütten. Zeit.*, 1890, 49, 150.

For poor ores the weight taken is 10 g., for richer ores 2 g., for fume 0·5 g.; 10 g. of hammer-scale is mixed with the sample by means of a glass rod, the mixture is covered with 10 g. of hammer-scale, and above this is added about 3 g. of zinc oxide.

R. Biewend[1] has considerably improved the Eschka assay. He advises that no more material shall be taken than will produce 0·2 g. of mercury. Instead of iron he uses copper filings; to aid in keeping back the heat from the gold amalgam, he recommends covering the mixture with calcined magnesia. The separation of the mercury is effected in two stages. The greater part is distilled off at the lowest possible temperature, then, after cooling, a second lid is put on and the crucible is heated to redness. To protect the lid from the heat of the flame, the crucible is placed in a hole cut in asbestos. Biewend found that the loss, even in the assay of pure cinnabar, did not exceed 0·2 per cent.

C. Ehrmann and J. Slaus-Kantschieder[2] found that the Eschka method was not suited to pyritic ores, and assayed Dalmatian ores of this character by heating in a current of chlorine.[3]

Amalgams.

The mercury in gold and silver amalgams is usually determined by distillation from glass or iron retorts, the gold or silver being subsequently cupelled and weighed, and the mercury ascertained by difference.

Dental amalgams are heated in a porcelain boat in a combustion tube in a current of hydrogen. About 1 g. of material is used, the tube heated quite gradually to a red heat, and the mercury determined by loss.

A similar method is employed for white metals (anti-friction metals) containing mercury.

Electrolytic Methods of Determination.

Several of these methods have been introduced in practice.

De Escosura[4] heated 0·5 g. of finely powdered ore in a porcelain dish with 10 to 15 c.c. of hydrochloric acid and 20 c.c. of water, 0·5 to 1 g. of potassium chlorate was added, a little at a time, and the heating continued until the cinnabar was completely dissolved; 50 c.c. of water was then added, and the free chlorine boiled off. Selenium and tellurium were precipitated by adding 20 c.c. of a saturated solution

[1] *Berg u. Hütten. Zeit.*, 1902, **61**, 441; *Chem. Zeit.*, 1903, **27**, 400.
[2] *Chem. Zeit.*, 1902, **26**, 201; *J. Soc. Chem. Ind.*, 1902, **21**, 501.
[3] Fresenius, *Quantitative Analysis*, 7th edition, vol. ii., p. 384.
[4] *Berg u. Hütten. Zeit.*, 1886, **45**, 329; *J. Chem. Soc. Abstr.*, 1886, **50**, 650.

of ammonium sulphite and boiling for a few minutes; after standing for half an hour, the precipitate was filtered off and washed until the filtrate amounted to about 200 c.c. The filtrate was electrolysed for twenty to thirty hours, using two Bunsen cells, a cathode of gold foil, and an anode of platinum foil; after the electrolysis was completed, the cathode was washed with alcohol, dried, and weighed. A number of assays can, of course, be carried out simultaneously by this method.

According to a more recent method of de Escosura, the ore may be electrolysed without previous solution; 0·2 g. of 10 per cent. ore is treated cold in a platinum dish with 10 c.c. of hydrochloric acid, 90 c.c. of water, and 20 c.c. of a cold, saturated solution of ammonium sulphite. The dish serves as the anode, and a piece of gold foil is used as the cathode.

This method is a modification of that due to Classen,[1] who treats the ores with water acidified with hydrochloric acid, or with a 10 per cent. solution of common salt, and adds ammonium oxalate. The mercury is then deposited on a matte platinum cathode placed in the solution.

According to Classen, about 0·3 g. of mercury can be deposited completely from the ammonium oxalate solution at ordinary temperatures, in from two to three hours, with an E.M.F. of 4 to 4·75 volts and a current density of 0·93 to 1·02 ampères per 100 sq. cm. of cathode surface.

Edgar F. Smith deposits the mercury from a potassium cyanide solution. To the oxidised solution containing about 0·2 g. of mercury, about 0·25 to 2 g. of potassium cyanide is added, the solution diluted to 175 c.c. with water, and electrolysed. According to Classen, the current density to be employed is 0·03 to 0·08 ampère per 100 sq. cm., and the E.M.F. 1·65 to 1·75 volts.

Brand[2] adds a slight excess of sodium pyrophosphate to the oxidised solution, dissolves the precipitate in aqueous ammonia or ammonium carbonate, and electrolyses with a current capable of producing 2 c.c. of electrolytic gas per minute; 1 g. of mercury can be deposited in five or six hours.

Rising and Lenker[3] dissolve cinnabar in a strong solution of hydrobromic acid, neutralise with sodium hydroxide, add potassium cyanide to the diluted solution (see E. F. Smith's method), and deposit the mercury on a platinum cathode by a very weak current.

Mercury may also be determined electrolytically by the use of a rotating anode with or without a mercury cathode[4] (*cf.* Copper,

[1] *Quantitative Chemical Analysis by Electrolysis*, 1919.
[2] *Z. angew. Chem.*, 1891, **4**, 202; *J. Chem. Soc. Abstr.*, 1890, **58**, 294.
[3] *J. Amer. Chem. Soc.*, 1896, **18**, 96.
[4] Cf. *Electro-analysis*, E. F. Smith, 1908.

pp. 170-7). With the rotating anode only, the whole of the metal in an electrolyte containing 0·5 g. of mercury, as mercurous nitrate, and 1 c.c. of nitric acid, made up to 115 c.c., may be deposited in ten minutes with a current of 7 ampères at 7 volts, the anode rotating 700 times per minute.

According to M. Perkin,[1] the determination of mercury electrolytically with a gold cathode, or with a rotating silver electrode, gives high results, and he considers that the best results are obtained with a rotating anode and a mercury cathode.

Examination of Mercury for Impurities.

If mercury, freed from fatty matter and dust by means of hot sodium hydroxide, does not exhibit a bright, convex surface, but fouls glass, and if about 1 c.c., shaken round in a large porcelain dish, leaves a tail of metal and shows dark-coloured streaks, it contains foreign metals, such as tin, lead, zinc, copper, bismuth, and cadmium.

To detect individual impurities about 20 g. is distilled in a glass retort until only about 1 g. remains, and the residue examined. After dissolving in hot nitric acid of sp. gr. 1·2, any meta-stannic acid is filtered off, after addition of water, the filtrate evaporated down with sulphuric acid to precipitate lead, and mercury, copper, and bismuth precipitated in the filtrate from the lead with sulphuretted hydrogen. Hot nitric acid dissolves the copper and bismuth from this precipitate; the presence of copper is shown by the blue colour obtained on the addition of excess of ammonia, and bismuth by the white precipitate of basic nitrate, obtained by boiling down the solution and then diluting with water. Zinc, cadmium, and iron can be detected in the filtrate from the precipitate obtained with sulphuretted hydrogen.

A method for the complete quantitative examination of mercury has been worked out by Fresenius.[2]

The Purification of Mercury.

Mechanical impurities, such as dust, grease, etc., may be removed by allowing the mercury to trickle into a tall cylinder, filled with a hot dilute solution of sodium hydroxide. After washing with water the metal is dried by means of a towel in a large porcelain dish and poured through a perforated filter paper until only about 1 c.c. remains behind. If the impurities consist of dissolved metals (lead, zinc, copper, tin, etc.), the purification may be effected chemically, by treating with acids, etc.

Thorough shaking of impure mercury with a nitric acid solution of mercurous nitrate dissolves the foreign metals; a mixture of chromic acid and sulphuric acid is also satisfactory as a purifying agent.

[1] *Trans. Faraday Soc.*, 1909-10, 5, 45; *J. Soc. Chem. Ind.*, 1909, **28**, 493.
[2] *Quantitative Analysis*, vol. ii., p. 379.

The following method, due to R. Finkener, as modified by Ulex, is especially satisfactory:—About 5 kg. of impure mercury is thoroughly shaken in a strong stoppered bottle of 2 litres capacity, with 250 c.c. of ordinary hydrochloric acid and 75 c.c. of a concentrated solution of ferric chloride. In three to six days, a subdivision of the mercury into tiny globules, covered with a layer of mercurous chloride, takes place. After treatment for several days, the contents of the bottle are washed into a large, strong porcelain dish of about 5 litres capacity and washed four times with 2 litres of hot water, acidified with hydrochloric acid, to remove lead chloride, etc., the washing being accompanied by thorough agitation. The dish is then placed on a heated water-bath, and a concentrated hydrochloric acid solution of 200 g. of fresh stannous chloride poured on to the mercury and the whole warmed and stirred, at the same time, with a porcelain spatula until the mercury has all run together; the mercury is then washed in the dish with running water, dried with clean towels, and filtered through a perforated filter paper.

The best method for freeing mercury from foreign metals is by distillation, the surface being covered with iron filings. The distillation is often carried out in vacuo; many forms of apparatus have been described for this purpose.[1]

COPPER

Wet methods are almost exclusively employed in the assaying of cupreous materials including all raw materials, the various classes of metallic copper and alloys. The dry methods are tedious, lengthy, and not accurate; reliable results are obtainable only in the assaying of ores containing native copper, such as the products dealt with at the smelting works of the Lake Superior district.[2] Both in England and in America the dry assay is occasionally taken as a basis for sales; in Germany the wet methods only are recognised.

The Cornish Dry Assay is an adaptation of metallurgical processes on a very small scale, to determine the amount of copper the smelter may expect to extract, and also to indicate any special difficulties that are likely to be met with in the refining of the metal extracted, rather

[1] *Cf.* Hulett, *Z. physik. Chem.*, 1900, **33**, 611; *J. Soc. Chem. Ind.*, 1900, **19**, 128; *cf.* also, *Z. angew. Chem.*, 1921, **34**, 359, 443.

[2] *Cf.* "Fire-Assay for Copper," G. L. Heath, *J. Amer. Chem. Soc.*, 1902, **24**, 699; *J. Chem. Soc. Abstr.*, 1902, **82**, 698.

than a method for the exact determination of the copper contents. The principal stages in this assay consist of—(1) the concentration of the copper in a regulus by fusion with suitable fluxes in a crucible; (2) the roasting of the regulus to convert the sulphides into oxides; (3) the reduction of the copper oxide by fusion with suitable fluxes and reducing agents to obtain crude copper; and (4) the refining of the copper obtained. Low results are invariably obtained by this method, the margin being generally from 1 to 5 per cent., as compared with the wet assay.

There are many different methods of wet assay, gravimetric, volumetric, and colorimetric, and the one adopted will depend on the character of the material, the time available, and the accuracy demanded.

The materials requiring to be assayed include the following :—

Copper Ores.

Ores.	Composition.
Native Copper.	
Sulphide Ores :—	
Chalcocite (chalcosine, copper glance)	Cu_2S
Erubescite (bornite)	Cu_3FeS_3
Copper pyrites (chalcopyrite)	$CuFeS_2$
Covelline (Indigo copper)	CuS
Fahl ores { Tetrahedrite	$Cu_6Sb_2S_6$
Fahl ores { Tennantite	$Cu_6As_2S_6$
Oxide Ores :—	
Cuprite (ruby copper ore)	Cu_2O
Tenorite (melaconite)	CuO
Malachite	$CuCO_3, Cu(OH)_2$
Azurite (chessylite)	$2CuCO_3, Cu(OH)_2$
Chrysocolla	a hydrated silicate
Atacamite	$CuCl_2, 3Cu(OH)_2$

The chief ore is copper pyrites, which frequently occurs in conjunction with lead and zinc ores, iron pyrites, stibnite, mispickel, etc.

Copper Matte (low grade and high grade).—This often requires to be assayed both in works and commercial laboratories. Copper mattes are complex mixtures of sulphides and may contain metallic copper; besides copper, silver, iron, lead, and zinc, they often contain small quantities of nickel, cobalt, tin, arsenic, antimony, etc.; in technical laboratories, as a rule, only the copper, lead, and silver require to be determined. In its purest form copper matte approximates very closely to the formula Cu_2S.

Copper Speiss.—This contains copper, silver, iron, nickel, etc., combined chiefly with arsenic and antimony.

Copper Slags.—These consist of *smelter slags*, which are essentially silicates of iron and earthy bases low in copper; *converter slags*, in which silicate of iron predominates, about 2 per cent. of copper being present; and *refinery slags*, which may contain from 20 to 50 per cent. copper as silicate.

Blister Copper.—This is impure furnace copper, containing from 95 to 98 per cent. copper, usually with silver and a little gold; the other impurities consist of iron, sulphur, lead, zinc, bismuth, nickel, arsenic, antimony, etc.

Cement Copper (copper precipitate) is the impure metal precipitated from solution by means of scrap or pig iron, and contains from 50 to 95 per cent. copper, generally associated with arsenic, graphite, and compounds of iron.

Tough Copper.—This is refined marketable copper, and contains, as a rule, over 99 per cent. of copper, a little arsenic, cuprous oxide, frequently silver, minute quantities of the foreign metals found in blister copper, and traces of sulphur, and occasionally selenium and tellurium.

Electrolytic Copper.—This is almost chemically pure, but sometimes contains traces of lead, sulphur, bismuth, antimony, and arsenic.

Alloys of Copper contain varying proportions of copper, tin, zinc, nickel, lead, aluminium, manganese, phosphorus, and arsenic as essential elements, and may contain small quantities of iron, sulphur, bismuth, antimony, cadmium, silver, and gold as impurities.

Copper residues, copper scale, sweepings, etc.

Liquors including solutions from various wet and electrolytic processes, mine waters, plating bath solutions, etc.

A. Gravimetric Methods of Analysis

In these methods the copper is either deposited electrolytically as metal, or is converted into a suitable compound such as the sulphide, oxide, or thiocyanate; the electrolytic method is the most widely used.

Solution of the Material.

Native copper is dissolved in nitric acid. Sulphide ores, such as copper pyrites, erubesite, chalcocite, covelline, fahl ores, etc., and copper mattes are very finely ground and heated with strong nitric acid, tartaric acid being added with fahl ores; or aqua regia (one volume nitric acid to two volumes hydrochloric acid) may be used. After all action has ceased, it is usual to add an excess of concentrated sulphuric acid and boil on the hot plate until sulphuric acid fumes begin to be evolved.

Malachite, azurite, tenorite, and atacamite dissolve easily in either hot dilute sulphuric acid or in hydrochloric acid; cuprite is dissolved by dilute nitric acid.

Copper silicates and slags are decomposed by long-continued boiling with 50 per cent. sulphuric acid and a little nitric acid, or, more rapidly, by warming with dilute sulphuric acid and potassium fluoride in a platinum dish, followed by ignition, to decompose the fluorides.

Copper slags which have been properly chilled on taking the sample and crushed to pass a 100-mesh sieve, are completely soluble in dilute hydrochloric acid when the proportion of silica is below 40 per cent. Slag is, therefore, sampled at the furnace by dipping a small iron rod into it, and plunging the rod immediately into a bucket of water, or by catching some of the slag in an iron ladle and pouring it into water. To obtain a hydrochloric acid solution of these slags a weighed portion of the finely divided sample is added to boiling water contained in a beaker and the whole stirred vigorously during the addition of the necessary hydrochloric acid in order to keep the slag in suspension. The stirring must be continued until there is no danger of gelatinised slag adhering to the bottom of the beaker; the solution should then be boiled for a few minutes.

Blister copper and tough copper are dissolved in nitric acid; sweepings, etc., are treated as above with nitric acid or with aqua regia, after the organic matter has been burnt off. Copper alloys are dissolved or decomposed by nitric acid.

1. The Electrolytic Determination of Copper.[1]

The general principles and methods of electro-analysis are discussed in Vol. I., pp. 92-115.

The method devised by Luckow[2] for the determination of copper and the various modifications subsequently introduced, depend on the quantitative precipitation of copper as a coherent and pure metallic deposit on a weighed platinum cathode.

Acid solutions of copper nitrate or sulphate are ordinarily used in practice.

The current required for the deposition can be obtained from primary or secondary batteries, from a lighting or power circuit, or from a small generator set, preferably working in conjunction with a storage battery. The factors determining the source of current are the number of determinations to be made daily, the availability of a lighting or power supply, and the cost of installation and current.

[1] An account of the methods for the electrolytic determination of copper is given in the following works on electrolytic analysis:—

Quantitative Chemical Analysis by Electrolysis, A. Classen, translated by W. T. Hall, 1919.
Practical Methods of Electro-Chemistry, F. M. Perkin, 1905.
Electro-Analysis, E. F. Smith, 1919.
Analyse des Métaux par Électrolyse, A. Hollard and L. Bertiaux, 1906.

[2] *Z. anal. Chem.*, 1869, **8**, 23.

If primary cells are used for the electrolysis, Bunsen, Grove or Daniell batteries may be employed. With two Bunsen cells, 20 cm. in height, four determinations, from solutions each containing from 0·5 g. to 1·0 g. of copper, can be carried out simultaneously in from six to eight hours, provided the solutions are of approximately the same copper content and contain about equal amounts of free nitric acid.

An ammeter and a voltmeter should always be inserted in the circuit, and adjustable resistances should be employed for the regulation of the current. The arrangement of the circuits with these necessary adjuncts has been described in Vol. I., pp. 92-115.

Platinum Apparatus and Stands.—The forms of electrodes vary considerably, according to the quantity of copper it is required to be deposited and the desired rate of deposition. For small quantities of copper and with slow deposition stationary electrodes are used, but where rapidity of deposition is required one of the electrodes is made to rotate by suitable motive power, or the liquid is stirred in other ways. Stationary electrodes may consist of a cylindrical cathode of platinum foil, and a platinum wire anode, for small quantities of copper; for larger quantities of copper, a large truncated cone is employed as cathode, with a positive electrode of thick wire (*cf.* Vol. I., Figs. 37-40, pp. 98-100).

When cylinder or cone cathodes are used the electrolysis can be carried out in presence of insoluble material, such as gangue, etc., which remains at the bottom of the containing vessel; such cathodes are, therefore, especially suitable for the deposition of copper from the unfiltered solution obtained by boiling down the sample of ore with nitric acid and sulphuric acid, followed by treatment of the residue with water.

Classen's platinum dish cathode is stamped or hammered from platinum foil containing about 10 per cent. of iridium. It weighs about 35 g., is 9 cm. in diameter, 4·2 cm. deep, and has a capacity of 250 c.c. The anode consists of a perforated platinum disc, 4·5 cm. in diameter, attached to a stout platinum wire. The dish, when in use, rests on three platinum contact points on a metal ring. The ring and support for the anode are capable of being adjusted on the thick glass stem of the stand (*cf.* Vol. I., Figs. 41-43, p. 100). With this arrangement the contents of the dish can be warmed by means of a small Bunsen flame, placed underneath; a piece of thin asbestos sheet, supported about 1 cm. below the dish, equalises the heat.

Losses of liquid through spitting, due to the ascending gas bubbles, may be avoided by covering the containing vessel with the two halves of a divided clock-glass, the straight edges being notched, by means of a small round file with turpentine as a lubricant, so as to take the wires of the cathode and anode.

Many methods[1] have been devised for the rapid determination of copper by the use of strong currents, high voltage, and in some instances hot solutions, in conjunction with rapidly revolving electrodes, in order to obtain compact and adhesive deposits of the metal. Either the cathode or the anode is made to revolve. When the latter method is used, the anode may be either a spiral wire or a small dish, 7 cm. in diameter and 3 cm. deep, containing slits perpendicular to the edge and a circular opening in the bottom; by this arrangement free circulation of the liquid is insured.

During the deposition of copper on a platinum dish cathode, the anode is made to revolve at a speed of from 600 to 700 revolutions per minute. A much more concentrated copper solution may be used than under the ordinary conditions of electrolysis, and it can be heated to near the boiling point. Slightly acid sulphuric or nitric acid solutions, or ammoniacal or alkaline cyanide solutions, may be used. In the acid solutions there should be about 1 c.c. of free sulphuric acid (1 : 10), or 0·5 c.c. of free nitric acid (1 : 1).

With sulphuric acid solutions, containing about 0·5 g. of copper diluted to 125 c.c., and heated nearly to boiling, the copper is deposited in about five minutes with a current of 10 to 15 ampères and an E.M.F. of 8 volts.

For the determination of copper in pyrites, etc., it is often convenient to use an ammoniacal solution, and the following method may be adopted. The finely divided ore is decomposed with nitric acid, the solution evaporated to dryness, the residue moistened with a few drops of nitric acid and diluted with water; the resulting solution is then heated and filtered into a weighed platinum dish, where it is mixed with an excess of ammonium hydroxide. The iron present is thus precipitated as hydroxide, but may be left in the dish. The anode is put in motion and the solution electrolysed. The thorough agitation of the solution by the anode prevents any of the ferric hydroxide becoming attached to the deposited copper. With a dilution to 125 c.c., a current of 9 ampères, and an E.M.F. of 8 volts, fifteen minutes are required for the deposition of about 0·5 g. of copper.

Rotating cathodes have found considerable application in works' practice, and the most convenient form consists of a cylinder made of platinum gauze as shown in Fig. 45. A convenient weight is about 15 g., and the central spindle is made of platinum hardened with iridium. The anode used in conjunction with this type of cathode is of about the same weight, and consists of a cylindrical framework of larger diameter than the cathode, made of strips of platinum foil attached to platinum wire rings. This is shown in Fig. 45, from which it will be seen that the platinum foil is bent at right angles

[1] Vol. I., pp. 102-108.

along its length in order to agitate the solution thoroughly. R. C. Benner[1] uses electrodes of sand-blasted platinum gauze.

Details of a compact form of apparatus for six- and ten-unit sets are given by J. L. Jones,[2] in which the platinum gauze electrodes are stationary, and the stirrers consist of tungsten rods having glass propeller screws fused on the ends.

The Process of Electrolysis.—If other metals besides copper are present, the nitrate solution should contain not more than 10 per cent.

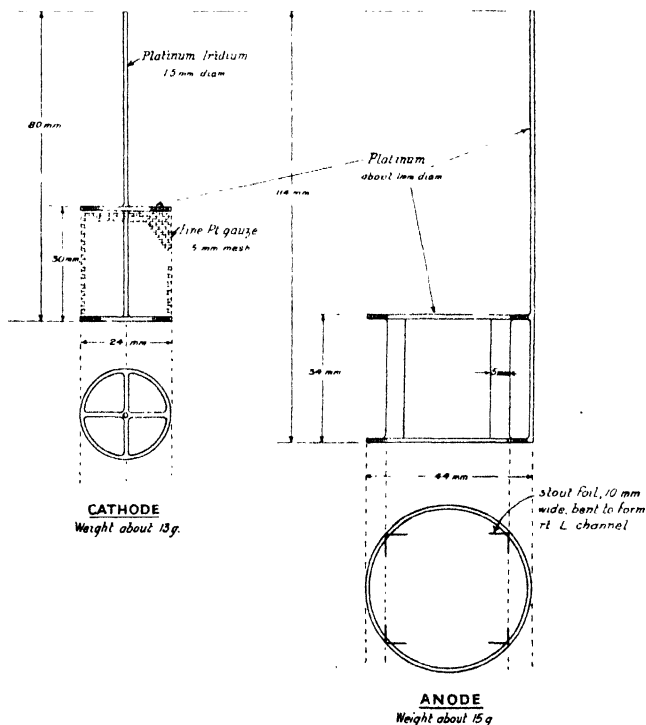



Fig. 45.

of free nitric acid of sp. gr. 1·2; for pure copper solutions 3 per cent. suffices. Sulphate solutions should contain preferably from 3 to 5 per cent. of free sulphuric acid and 0·5 per cent. of free nitric acid of sp. gr. 1·2. If free nitric acid is not present, the copper is likely to be deposited in a spongy form, when it does not adhere satisfactorily to the cathode, and some is lost in washing.

In the analysis of most copper alloys, after separation of tin and evaporation of the nitrate solution with sulphuric acid to precipitate

[1] *Chem. and Met. Eng.*, 1911, 9, 141.
[2] *Proc. Amer. Electrochem. Soc.*, 1917, 32, 329.

lead, a sulphate solution is obtained, which is suitable not merely for the deposition of the copper, but also for the subsequent separation of the zinc or nickel. A large excess of nitric acid must then be avoided, as it is largely converted into ammonium nitrate during the electrolysis. This salt interferes with the precipitation of nickel from the solution containing excess of ammonia, and also hinders the quantitative precipitation of zinc by sulphuretted hydrogen from the neutralised and diluted solution.

Stationary Electrodes.—Warming copper solutions to about 30° aids the deposition very considerably. The distance of the electrodes from each other should be 5 mm. in weak solutions, and 10 mm. in stronger solutions.

Using a current of from 1 to 1·5 ampères per 100 sq. m. of cathode surface, and an E.M.F. of from 2·2 to 2·7 volts, the complete deposition of 1 g. of copper should occupy from six to seven hours if the electrodes are stationary; with a weaker current the deposition is correspondingly slower. A test must always be made after the electrolysis, to ascertain whether the deposition is complete. The solution is diluted by the addition of 10 to 20 c.c. of water, and the electrolysis continued for a further thirty to sixty minutes. If during this time no sign of copper is observable on that part of the cathode not previously covered by the liquid, the deposition may be considered complete, although traces of copper may still be present in solution.

After deposition of the copper, the acid liquid is removed by means of a syphon and replaced with pure water until litmus paper indicates only a faintly acid reaction. The current is then switched off and the apparatus disconnected.

The solution and washings are treated with sulphuretted hydrogen, and any precipitate formed is collected and the copper present determined colorimetrically (p. 187) and added to the weight found on the cathode. The difficulty of depositing the last traces of copper from solutions containing nitric acid when using stationary electrodes is attributed by J. H. Stansbie[1] to nitrous acid which may be produced during electrolysis, but the addition of urea[2] overcomes this difficulty.

The cathode is quickly immersed in a large beaker of water, then removed and given a second washing, placed on a filter paper for a minute or so to drain, and then dipped into a beaker of absolute alcohol and allowed to drain again on filter paper. The electrode is then dipped into a beaker of ether and dried in a steam oven, cooled in a dessicator and weighed. The anode must also be washed, the washings being added to the main bulk of solution. The electrode may be cleaned and made ready for another determination by

[1] *Trans. Faraday Soc.*, 1913, 9, 11.
[2] E. Gilchrist and A. C. Cumming, *Ibid.*, 1913, 9, 186.

immersing it in strong nitric acid. The weights of the cathodes should be checked regularly.

If a dish is used as the cathode, it is removed from the stand, quickly washed three times successively with 10 to 20 c.c. of water, then once with 10 c.c. of absolute alcohol, and finally with ether and dried at 100°. If the apparatus is rapidly disconnected in, say, a quarter of a minute, the syphoning off of the liquid referred to above and the accompanying dilution may be dispensed with, for not more than a few tenths of a milligram of copper will dissolve in so short a time. The great advantage gained is that succeeding operations, such as the electrolytic separation of nickel, can be effected without first evaporating down the diluted solutions. Previous to the electrolysis, cylinders and cones must be handled by the wire only, dishes and crucibles on the outside only, as otherwise any greasy matter from the skin may prevent the deposition of the copper on the parts touched.

Rotating Electrodes. When rotating electrodes as described on p. 172 are used the solution of the copper alloy or ore in nitric acid is evaporated to a syrupy consistency, diluted with boiling water and filtered from tin, etc., which is washed with 5 per cent. nitric acid. The solution is cooled and electrolysed in a beaker of about 150 c.c. capacity. The cathode is revolved at about 300 revolutions per minute; the deposition of 0·8 g. copper with a current of 2 amps. at 10 volts. takes one hour. Small quantities of lead present may be determined by weighing the lead peroxide deposited on the anode.

Use of a Mercury Cathode and Rotating Anode for the Electrolytic Deposition of Copper.[1] A cup-shaped cell is used having a platinum wire fused through the bottom or the side near the bottom. A layer of mercury is introduced into this cup to cover the platinum wire, and the whole is weighed. This cup is then placed on a plate of sheet copper connected to the negative terminal of a battery, the outside part of the platinum wire being in direct contact with the copper; the mercury thus becomes the cathode. The anode may be of any form which can conveniently be rotated (*cf.* Fig. 47, Vol. I.).

The sulphate solution of copper, acidified with a few drops of sulphuric acid, is now introduced, and the revolving anode suspended from the rotator. The more concentrated the solution, the more rapidly will the copper be deposited, but the current should be continued several minutes after the solution becomes colourless, as the last traces of metal separate slowly. A current of about 5 ampères at a pressure of 6 volts should be used. When the metal has been completely deposited, the rotation of the anode is stopped, the cell

[1] Cf. Vol. I., p. 108; *Electro-Analysis*, E. F. Smith, 1908, pp. 77 *et seq.*; T. Slater Price, *J. Soc. Chem. Ind.*, 1909, **28**, 117.

filled with water, which is then syphoned off to the level of the anode and again filled up; this washing is continued until the wash water is free from acid. The wash water must always be tested for copper by means of sulphuretted hydrogen. The current is then interrupted and the amalgam thoroughly washed with water, then twice with absolute alcohol, and twice with ether. The cell containing the amalgam is then wiped dry on the outside, and, after the volatilisation of the ether, placed in a desiccator and subsequently weighed.

Influence of other Metals and Non-Metals on the Deposition of the Copper.—*Zinc*, *Nickel*, *Cobalt*, and small quantities of *Iron* in the copper solution do not interfere; if much iron is present, the ferric salts already in solution or formed during electrolysis tend to dissolve the deposited copper. To avoid this, the solution must be considerably diluted, and an increased current density employed for the electrolysis; it is better, however, to precipitate the copper first with sulphuretted hydrogen from a sulphate solution, gently ignite the copper sulphide obtained, dissolve it in nitric acid and electrolyse the resulting solution.

Lead should always be removed as sulphate when over 2 per cent. is present. From the nitrate solution, it will be deposited on the anode, as the dark brown hydrated peroxide, which may be weighed and the lead present calculated therefrom.

Manganese is not deposited from solutions containing more than 3 per cent. of nitric acid, but gives the violet coloration due to permanganic acid; from sulphate solutions it is precipitated as the dark brown hydrated peroxide, which only partially adheres to the anode and mainly floats in the liquid as a flocculent precipitate.

Mercury is deposited with the copper and is best removed by igniting or roasting the ore sample, etc., before dissolving it.

Silver and *Bismuth* are also deposited with the copper, the former partly as peroxide on the anode. The silver should be precipitated from the solution by adding just the necessary amount of sodium chloride solution, the silver chloride being filtered off before electrolysis. If an ore is first treated with aqua regia and then with sulphuric acid the silver remains as chloride with the insoluble matter on the filter paper. Bismuth is subsequently determined in the deposited copper, by the method described on p. 209 *et seq.*, and its amount deducted from that of the copper found.

Tin and practically the whole of the *Antimony* are removed in the initial treatment of the sample with nitric acid. *Antimony* and *Arsenic* deposit to a slight extent with the copper, but the greater portion comes down as a black coating on the copper, after this is all deposited. Small quantities of arsenic and antimony produce peculiar black comma-like vertical streaks on the copper, and if much arsenic and

antimony are present, they float as a black flocculent precipitate in the liquid. When more than traces of these elements are present, the copper should be separated previous to determination by electrolysis; arsenic, antimony, and tin may be separated from an impure copper sulphide precipitate by digestion with yellow sodium sulphide solution.

Arsenical and antimonial ores, copper speisses, etc., are very finely powdered and fused, in a covered porcelain crucible over a small Bunsen flame, with six times their weight of a mixture of equal parts of sulphur and anhydrous sodium carbonate, or six times their weight of anhydrous sodium thiosulphate; the heating is continued as long as sulphur is given off, the cooled melt extracted with boiling water, the residue washed with well-boiled hot water, containing a little ammonium sulphide, and then warmed with nitric acid, evaporated down with sulphuric acid, and treated as above.

2. Determination of Copper as Cuprous Sulphide.

This method depends on the precipitation of the copper as sulphide from a warm, strongly acid solution of the sulphate or chloride or from a cold dilute nitric acid solution by means of sulphuretted hydrogen. The voluminous greenish black precipitate is washed with water containing sulphuretted hydrogen and a trace of sulphuric acid, dried, the filter paper incinerated in a Rose's crucible, with subsequent addition of the copper sulphide and a few decigrams of sulphur, the whole gently and finally more strongly heated for twenty to thirty minutes in a current of pure dry hydrogen, allowed to cool in hydrogen, and the greyish black crystalline cuprous sulphide weighed; it contains 79·86 per cent. copper.

Hampe states that the weight of the cuprous sulphide should not exceed 0·2 to 0·3 g., as larger quantities of cupric sulphide cannot be completely converted into cuprous sulphide when heated in hydrogen. F. L. Halm[1] finds that by using a mixture of sulphuretted hydrogen and hydrogen, the proportions of which may vary within wide limits, more satisfactory results are obtained than by using hydrogen alone.

The method is particularly suitable for the separation of copper from solutions which contain no metals precipitated by sulphuretted hydrogen from acid solutions (lead, bismuth, cadmium, arsenic, antimony, tin); it thus effects the separation of copper from zinc, nickel, cobalt, manganese, aluminium, and iron.

Any mercury and arsenic which may be contained in the precipitate are volatilised during the ignition in hydrogen. If much arsenic is present, repeated heating with sulphur is necessary.

[1] *Z. anorg. Chem.*, 1917, **99**, 201. *J. Soc. Chem. Ind.*, 1917, **36**, 1290.

The dilute solution must be strongly acid to ensure that zinc is not precipitated; 500 c.c. of the solution should contain preferably from 75 to 100 c.c. of free hydrochloric acid, or 10 c.c. of free sulphuric acid. The precipitation is effected in a covered beaker, at about 70°, and a rapid current of sulphuretted hydrogen is passed into the solution until the precipitation is complete. The precipitate is washed with very dilute sulphuretted hydrogen water acidified with sulphuric acid; any hydrochloric acid remaining in the precipitate may cause a loss of copper, through volatilisation as chloride during the subsequent heating.

As the process is tedious and lengthy it is seldom used for technical purposes, volumetric methods being preferred.

3. Precipitation of Copper with Sodium Thiosulphate.

The use of an aqueous solution of sodium thiosulphate as a substitute for sulphuretted hydrogen in qualitative analysis was first introduced by G. Vortmann[1] and A. Orlowski,[2] and was subsequently used by them for the quantitative separation of copper, the copper being finally weighed as cuprous sulphide. Vortmann also recommended it for the separation of copper from cadmium, which is not precipitated by sodium thiosulphate in acid solution. H. Nissenson and B. Neumann[3] have modified and considerably simplified the method by converting the cupric sulphide into copper oxide by roasting in a porcelain crucible and weighing the oxide as cupric oxide. This method of separation is more useful, however, as a preliminary treatment for volumetric determination.

The following is the procedure adopted by Nissenson and Neumann for the analysis of copper mattes and copper-lead mattes, which contain a considerable amount of iron and frequently zinc and arsenic, in addition to copper, lead, and sulphur. One gram of the finely powdered sample is dissolved by heating with 7 to 10 c.c. of nitric acid of sp. gr. 1·4, in an Erlenmeyer flask, and the solution, after addition of 10 c.c. of sulphuric acid, evaporated until white fumes of sulphuric acid are given off; the cooled residue is taken up with water, and silver precipitated by the addition of a few drops of hydrochloric acid. After thorough cooling, the lead sulphate, silica, and silver chloride are filtered off, washed with water containing 1 per cent. of sulphuric acid, and finally with distilled water. For the further treatment of the impure lead sulphate, *cf.* Lead, p. 226. The filtrate is boiled in a porcelain dish, with about 5 g. of sodium thiosulphate, until the copper sulphide settles well; this is then filtered off, washed

[1] *Z. anal. Chem.*, 1881, **20**, 416.
[2] *Ibid.*, 1882, **21**, 215; *J. Chem. Soc. Abstr.*, 1882, **42**, 1232.
[3] *Chem. Zeit.*, 1895, **19**, 1591, 1592; *J. Chem. Soc. Abstr.*, 1896, **70**, 450.

well with hot water, the filter with precipitate transferred to a sufficiently large porcelain crucible, dried, and the whole then placed in a moderately hot muffle; the temperature of the muffle must not be too high, as cupric oxide is partially converted into the suboxide at a high temperature.[1] The filter burns and the cupric sulphide is gradually converted into cupric oxide; any sulphate formed as an intermediate product loses its sulphuric acid completely on heating. After the first weighing, the crucible is again strongly heated in air, and this is repeated until a constant weight is attained. The results obtained by this modified process agree extremely well with those obtained by electro-deposition.

4. Precipitation of Copper as Thiocyanate [Cu(CNS)] (Rivot's Method.)

An aqueous solution of potassium or ammonium thiocyanate gives, with neutral or nearly neutral solutions of cuprous salts, an almost white precipitate of cuprous thiocyanate; the precipitation is complete in the course of several hours. Zinc, cadmium, iron, nickel, cobalt, bismuth, tin, arsenic, and antimony are not precipitated, and consequently Hampe[2] introduced the method for the analysis of commercial copper. The cuprous thiocyanate is somewhat soluble in an excess of the precipitant, but only very slightly soluble in pure water.

To carry out the determination, the acid nitrate or sulphate solution of ore, furnace product, or alloy, from which the lead and silver have previously been separated, is neutralised with sufficient sodium hydroxide to produce a permanent precipitate, saturated with sulphur dioxide in the cold, then warmed to 40°, and sulphur dioxide again passed. Precipitation is then effected by the gradual addition of a solution of potassium thiocyanate of known strength. One cubic centimetre of a solution containing 76·5 g. potassium thiocyanate per litre will precipitate 0·05 g. of copper. Since cuprous thiocyanate is soluble to a certain extent in an excess of the precipitant, care must be taken to use the least possible excess. After standing for about four hours, the precipitate is collected on a good filter paper or Gooch crucible and washed with cold water. If the filter paper has been previously dried at 100° to 105° and weighed, the weight of the copper thiocyanate can be ascertained after drying for four hours in an air-bath at 100° to 105°. It may save time, however, to convert the thiocyanate into cuprous sulphide. To effect this the filter and precipitate are dried rapidly, the filter burnt in a Rose's crucible, and the thiocyanate added and ignited, proceeding from this stage as described on page 177.

[1] *Cf.* Bailey and Hopkins, *J. Chem. Soc.*, 1890, **57**, 269.
[2] *Chem. Zeit.*, 1893, **17**, 1691; *J. Soc. Chem. Ind.*, 1894, **13**, 421.

In presence of much iron (as, for example, in the solution from copper pyrites), a blood-red coloration is at first produced on the addition of the thiocyanate; this gradually disappears through the action of the sulphur dioxide.

The metals mentioned above may be determined in the filtrate by first evaporating down, decomposing the slight excess of thiocyanate by heating with nitric acid, and then following the usual analytical methods.

On account of the tardy quantitative precipitation of the thiocyanate and its appreciable solubility in water and in excess of potassium thiocyanate, this method is not so much used as the previously described gravimetric methods.[1]

5. Precipitation of Copper with "Cupferron" (Nitrosophenylhydroxylamine).

O. Baudisch[2] has proposed the use of the ammonium salt of nitrosophenylhydroxylamine, $C_6H_5.N(NO).OH$, under the name of "Cupferron," as a precipitant for copper, and as a means of separating it from nickel, cobalt, aluminium, and chromium. The method has also been investigated by H. Biltz and O. Hödtke.[3]

The reagent is employed in 6 per cent. aqueous solution, which can be kept for some weeks without material alteration, and which should be filtered if it has become turbid.

The precipitation is best carried out in acetic acid solution, or in mineral acid solution, mixed with the corresponding quantity of sodium acetate; any considerable quantity of free mineral acid dissolves the copper compound and prevents its quantitative separation. A considerable excess of the reagent, double the calculated quantity, is employed. Since the bright grey copper precipitate closely resembles the colour of the solid reagent, the completion of the precipitation cannot be clearly recognised until the precipitate has settled The precipitate is filtered off on the pump, washed first with faintly acidified water, then with 1 per cent. sodium carbonate solution to remove the excess of the reagent, and then finally with water. The filter and the dried precipitate are carbonised in a covered crucible, and then ignited, with free access of air, or in a current of oxygen, to cupric oxide. The separation of copper from zinc is effected in acetic acid solution, that from cadmium only in mineral acid solution.

[1] For a recent investigation of the method, see Fenner and Forschmann, *Chem. Zeit.*, 1918, 42, 205.

[2] *Chem. Zeit.*, 1909, 33, 1298; *J. Soc. Chem. Ind.*, 1910, 29, 115.

[3] *Z. anorg. Chem.*, 1910, 66, 426; *J. Soc. Chem. Ind.*, 1910, 29, 721.

B. Volumetric Methods of Analysis

Of the volumetric methods described below, the cyanide method is suitable for mine and smelter samples when great accuracy is not essential; the iodide method is applicable in all cases and is capable of giving results as accurate as those obtained by the electrolytic method.

1. Parkes' Potassium Cyanide Method.[1]

This method is based on the decoloration of blue ammoniacal cupric solutions by potassium cyanide with the formation of colourless, soluble potassium copper cyanides.

The potassium cyanide solution is prepared by dissolving 20 g. of the purest commercial potassium cyanide in 1 litre of water. It is standardised by a cupric solution containing approximately the same amount of copper as the solutions to be titrated, dissolved in 5 c.c. of nitric acid, diluted to 200 c.c., neutralised with ammonia, until the bluish-green hydrate is precipitated, after which 20 c.c. of ammonia (1 : 1) is added. For the standardisation, the cyanide solution is run from a burette into the copper solution, contained in a flask, until the solution assumes a faint violet tinge, the solution having been agitated during the addition of the cyanide. After standing for a couple of minutes decoloration should be complete; if, however, any colour remains, a further few drops of cyanide solution are added.

Satisfactory results can be obtained only if each series of titrations is carried out under similar conditions as to temperature, time occupied, and the amount of copper, ammonia, and ammonium salts present.

As lead, bismuth, silver, nickel, cobalt, manganese, zinc and large quantities of calcium interfere, these should be removed from the solution before titration, or the copper should be precipitated as metal or as sulphide and redissolved. When more than 0·5 per cent. of arsenic (in the absence of iron) or antimony is present, these also should be removed.

The precise manner of carrying out the method varies with the nature of the material. For pure or known materials, it is conducted as follows:—From 0·5 to 1 g. of the finely powdered material is weighed into a small flask and decomposed with 10 c.c. of nitric acid; in some cases a little hydrochloric acid may also be used. When thoroughly decomposed, a little water is added, then ammonia until neutral, and an excess of 20 c.c. of ammonia (1 : 1). The whole is diluted to 200 c.c., cooled in running water, and then titrated with the cyanide solution to complete decoloration. The ferric hydroxide may often be left in the solution and allowed to settle after each addition of cyanide, but when it interferes with the end-point, it may be filtered off when only a faint

[1] *Cf.* Balling, *Probierkunde*, 1879, p. 274.

blue coloration remains in the solution. Many prefer to filter off the iron before commencing the titration, but the precipitate must then always be redissolved and reprecipitated, the second filtrate being added to the first, as the ferric hydroxide invariably carries down some copper.

The copper in impure or unknown materials must be separated before titration. This may be effected either by means of sulphuretted hydrogen, sodium thiosulphate, or metallic aluminium. The first two methods are described on pp. 177-8. The precipitate of copper sulphide is dissolved in nitric acid, and the solution treated as described above.

The method of separation on metallic aluminium is very largely used, both for the cyanide method of assay and also for the iodide method described below. After decomposing the sample with nitric acid, 10 c.c. of sulphuric acid is added, and the whole heated until dense white fumes of sulphuric acid have been evolved for some minutes. The solution is then cooled, diluted to 50 c.c., a bent piece of aluminium foil, $\frac{1}{16}$ in. thick and about 1 in. by 3 in. added, and the whole boiled briskly until all the copper is precipitated. The presence of a minute trace of sodium chloride will assist this precipitation. The whole of the copper should come down in from five to ten minutes, and should not adhere to the aluminium ; this occurs only if the piece has become pitted by being used a number of times. The aluminium is removed and washed, and the precipitated copper washed by decantation several times, filtering the decanted liquor each time. When the washing is completed, the filter paper should be opened and any adhering copper washed back into the main precipitate by means of a fine jet of water from a wash-bottle, followed by a few drops of nitric acid, and a further washing. It is then dissolved in 5 c.c. strong nitric acid, the solution made alkaline with ammonia, and titrated as above. After separation on aluminium, the residual solution should always be tested for copper by means of sulphuretted hydrogen.

2. De Haen's Iodide Method, as modified by Low.

The de Haen[1] iodide method for the determination of copper, as modified by Low,[2] is widely used commercially, both in England and in America. Low is of opinion that it is better than the electrolytic method both as regards accuracy and rapidity.

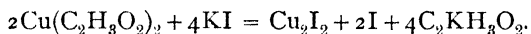
The determination is carried out as follows:—A solution of sodium thiosulphate, containing 38 g. of pure thiosulphate to the litre, is standardised with copper. Chemically pure copper (0·2 g.) is dissolved

[1] *Ann. Chem. Pharm.*, 1873, **91**, 237. The method was first described by E. O. Brown, *Quart. J. Chem. Soc.*, 1857, **10**, 65.

[2] *Eng. and Min. J.*, 1895, **59**, 124 ; *J. Soc. Chem. Ind.*, 1895, **14**, 304 ; *cf.* also, Westmoreland, *J. Soc. Chem. Ind.*, 1886, **5**, 48.

in 4 c.c. of concentrated nitric acid in a flask of about 250 c.c. capacity, the solution boiled down to 1 or 2 c.c., 5 c.c. of water added, then 5 c.c. of strong ammonia, and the whole boiled for a minute. The boiling is absolutely necessary, as otherwise the liquid reacts with potassium iodide as though it contained free nitric acid. Six c.c. of acetic acid is then added and 40 c.c. of cold water; the solution is thoroughly cooled, 3 g. of potassium iodide added, and allowed to dissolve.

The reaction is represented by the following equation; cuprous iodide is precipitated and iodine liberated:—

$$2Cu(C_2H_3O_2)_2 + 4KI = Cu_2I_2 + 2I + 4C_2KH_3O_2.$$

The thiosulphate solution is run into the copper solution containing the liberated iodine from a burette until the colour is only pale yellow, when starch solution is added until blue; the titration is then continued to decoloration in the usual manner (*cf.* Vol. I., pp. 69-72).

The starch solution must be made fresh every two days, by agitating 0·5 g. of rice starch with 250 c.c. of cold water, and then heating to boiling. Better results are obtained by using soluble starch and adding a few drops of chloroform to the solution which will then keep much longer. The thiosulphate solution, made by dissolving pure sodium thiosulphate in pure boiled water, free from air, keeps for a month without change.

The possible interference of nitrous acid in this determination is avoided by M. E. Pozzi-Escot[1] by adding an excess of urea before the addition of ammonia to the solution.

Low adopts the following method for ores:—One gram of the finely powdered sample is treated with 10 c.c. of concentrated nitric acid, in a flask of about 250 c.c. capacity; the resulting solution is evaporated nearly to dryness, and the residue boiled for two or three minutes with 10 c.c. of concentrated hydrochloric acid; 10 c.c. of concentrated sulphuric acid is then added, and the boiling continued until fumes of sulphuric acid are evolved.

The cooled residue is treated with 10 c.c. of water, boiled and filtered from lead sulphate, gangue, sulphur, etc., into a shallow beaker of 8 cm. diameter. The copper is precipitated on aluminium and dissolved in nitric acid as described on p. 182. It is usual to add 0·5 g. of potassium chlorate in order to oxidise any arsenic to arsenic acid, and to boil down the liquid to 1 to 2 c.c.; no basic salts of copper should separate during this concentration. The titration is then carried out as in the standardisation described above.

Since 1 g. of pure copper requires 5·22 g. of potassium iodide, 3 g. of potassium iodide will suffice for 1 g. of all ores containing less than 50 per cent. of copper. For very rich ores, 5 g. of potassium iodide should be used.

[1] *Ann. Chim. anal.*, 1913, **18**, 219.

Arsenic, as arsenic acid, does not interfere with the determination; bismuth, by reason of the deep yellow colour of potassium bismuth iodide, may cause the addition of starch to be made at too late a stage, though this does not frequently happen. Lead also changes the appearance of the end-point to a certain extent; ferric salts must be absent or may be precipitated as ferric phosphate[1] by the addition of sodium phosphate to the solution. The ferric phosphate precipitate does not react with potassium iodide.

Instead of neutralising with ammonia, as described in Low's method, many chemists prefer to use sodium carbonate. This should be added in very slight excess only, followed by the addition of acetic acid. If a large excess of sodium carbonate be used, the sodium acetate formed interferes to a certain extent with the titration. Powdered marble may be used with advantage for the neutralisation, as an excess does not interfere. Another method which is much used is to add an excess of zinc acetate to the nitric acid solution, by which means zinc nitrate is formed and acetic acid liberated. This is a very quick, clean, and reliable method of treatment.

The iodide method gives results which agree very closely with the electrolytic assay. It is used especially for controlling the sales of copper ores, mattes, etc., and in the analysis of alloys when it is impracticable to use the electrolytic method.

3. Stannous Chloride Method.

This method is based on the reduction of cupric to cuprous chloride by stannous chloride. A hydrochloric acid solution of stannous chloride is added to the hot, deep green hydrochloric acid solution, containing cupric chloride and free from oxidising or reducing agents, until the green colour has disappeared. One drop of a concentrated solution of mercuric chloride should produce a very faint precipitate of mercurous chloride when the titration is finished. The end-point corresponds with the complete decoloration of the liquid, and in a good light it is quite sharp. Balling,[2] who has examined the method very carefully, found the differences between results given by it and by gravimetric methods not to exceed 0·1 to 0·2 per cent.

The stannous chloride solution is prepared by dissolving 6 g. of pure tin, or the corresponding quantity of freshly prepared commercial stannous chloride, in 200 c.c. of pure 25 per cent. hydrochloric acid, and diluting to a litre with cold, boiled water. It is kept in quantities

[1] H. Ley, *Chem. Zeit.*, 1917, 41, 763.

[2] *Die Probierkunde*, 1879, pp. 265 *et seq.*; tables for the calculation of the copper content are given on pp. 270 *et seq.*

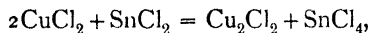
of 3 litres or more in a stock bottle connected with a small carbon dioxide generator to prevent oxidation.

A copper solution of known strength is prepared by weighing out 2 g. of electrolytic copper which is dissolved in 8 c.c. of nitric acid of sp. gr. 1·4, the solution evaporated with 2 c.c. of sulphuric acid to remove nitric acid completely, the residue taken up with water, and made up to 500 c.c.

To standardise the stannous chloride solution, 25 c.c. of the copper solution, corresponding to 0·1 g. of copper, is run into a flask of 200 c.c. capacity, 5 c.c. of pure concentrated hydrochloric acid added, and the mixture brought to the boil, when stannous chloride solution is run in, from a freshly filled burette, until the green colour of the boiling solution is discharged. Any greenish tinge appearing on the addition of a further 5 c.c. of concentrated hydrochloric acid should be discharged by one drop of stannous chloride solution. The stannous chloride solution must be restandardised about once a week.

The copper in ores is determined as follows:—From 2 to 5 g. of the finely powdered sample, according to its richness in copper, is boiled in a flask with aqua regia, and then evaporated nearly to dryness with sulphuric acid. On taking up with water and filtering, gangue, lead sulphate, and silver chloride remain on the filter paper; the filtrate is diluted to 250 c.c., of which 25 c.c. is run into a flask and treated with 5 c.c. of concentrated hydrochloric acid, etc., as above.

Iron is almost always present and then the hydrochloric acid solution is of a yellowish green colour, and the stannous chloride used corresponds to the total of copper and iron. To determine the iron, a separate portion of 25 c.c. of the sulphate solution is warmed with granulated zinc, the clear solution poured off from the precipitated copper, the copper washed by decantation with water, and the combined solutions, after cooling, titrated with potassium permanganate. The same quantity of stannous chloride is required for 55·85 parts of iron as for 63·57 parts of copper, in accordance with the following equations:—

$$2CuCl_2 + SnCl_2 = Cu_2Cl_2 + SnCl_4,$$
$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

For the subsequent determination of the copper, it is better to dissolve completely the excess of zinc (which must be free from lead) by warming with dilute sulphuric acid, decanting, then adding a sufficiency of nitric acid to dissolve the copper, and boiling down with sulphuric acid to remove nitric acid. The residue is dissolved in water, hydrochloric acid added, and the liquid titrated as above.

Any antimonic acid or antimony chloride in solution is reduced by the stannous chloride to antimonious chloride, and this causes high results.

Arsenic has no effect on the assay. Nickel and cobalt must be previously removed. In the presence of iron, antimony, nickel and cobalt, it is best to precipitate the copper with sodium thiosulphate (p. 178), treat the sulphide with nitric acid and sulphuric acid, and then titrate the sulphate solution in presence of hydrochloric acid.

The process is frequently used, especially where a stannous chloride solution is also used for the titration of iron.

4. Ammonium Thiocyanate Method.

This method consists in the precipitation of the copper as cuprous thiocyanate from a nearly neutral hot solution, saturated with sulphur dioxide (*cf.* also, p. 179). A slight excess of a measured solution of ammonium thiocyanate of known strength is used for the precipitation, the excess being titrated back, in the cold, with silver nitrate solution, in presence of ferric sulphate and nitric acid.

Any silver, mercury, chlorine, bromine, iodine, or cyanogen present interferes with the process, and another method should then be used.

To carry out the determination, the nitric acid or sulphuric acid solution of the sample is first nearly neutralised with sodium carbonate or sodium hydroxide, free from chlorine; for about 0·5 g. of copper approximately 50 c.c. of a saturated aqueous solution of sulphur dioxide is then added, the whole heated to boiling and precipitated with an excess of an ammonium thiocyanate solution standardised by silver nitrate (*cf.* Vol. I., p. 73). (As 107·88 parts of silver require the same amount of ammonium thiocyanate for precipitation as 63·57 parts of copper, the silver titre must be multiplied by $\frac{63 \cdot 57}{107 \cdot 88} = 0 \cdot 5893$.)

It is convenient to use a 500 c.c. flask for these operations, or else to wash the total liquid, after cooling to the ordinary temperature, into a flask of this size, and to dilute to the mark, mix, allow to stand for a short time, and then filter an aliquot portion through a dry filter paper into a dry beaker.

One hundred cubic centimetres of the filtrate is then treated with 5 c.c. of a cold saturated solution of iron alum and a few drops of pure nitric acid, and the solution titrated with a standardised silver nitrate solution, until the ferric thiocyanate colour is discharged. The amount of thiocyanate used for the precipitation of the copper is thus obtained.

The determination of copper in blister copper, alloys, mattes, and ores, the copper content of which is approximately known, can be carried out in a short time by this method, and the results are sufficiently accurate for technical purposes. The error introduced by not taking account of the volume of the solid cuprous thiocyanate is negligible.

5. Potassium Permanganate Method.[1]

This method consists in the precipitation of the copper as cuprous thiocyanate and the subsequent decomposition of the precipitate with sodium hydroxide solution so as to form sodium thiocyanate which is acidified with sulphuric acid, and the liberated thiocyanic acid titrated with standard potassium permanganate solution.

The cuprous thiocyanate precipitate is obtained as described under the gravimetric method (p. 179), and in this method it is preferably collected on a pulp filter, and washed thoroughly with cold water.

The precipitate is then treated by pouring on a boiling 8 per cent. sodium hydroxide solution and washing thoroughly with hot water. The alkaline filtrate is acidified with dilute sulphuric acid and titrated with permanganate solution which has been standardised by means of pure copper.

C. Colorimetric Methods

The object of these methods is the determination of the copper content of definite volumes of blue ammoniacal cupric solutions by comparison with the colour of standard solutions containing known quantities of copper. As in all colorimetric methods, it is taken for granted that the colour intensity of equal columns of solution is directly proportional to the amount of colour-producing material in the liquid. (*Cf.* Colorimetry, Vol. I., p. 179 *et seq.*)

The colorimetric determination of copper was originally recommended by Jacquelin, von Hubert, and others for rich as well as poor ores, graduated tubes being employed, such as are used in the Eggertz colorimetric determination of carbon in steel (*cf.* p. 48); the method is now employed only for the assay of poor ores, furnace products, and slags, the copper content of which does not exceed 1 per cent. and for the last traces of copper left in solution after the electrolytic deposition of copper as described on p. 170 *et seq.*

Strongly coloured solutions are very difficult to compare; and when considerably diluted and the content then ascertained by comparison with the standard solution, it is necessary to multiply by the dilution factor, and so the experimental error becomes increased to a corresponding degree.

An ammoniacal solution, prepared from the ore with nitric acid, must be compared with a standard solution prepared from copper nitrate, and a solution made with sulphuric acid must be compared with a copper sulphate solution, the colours of the ammoniacal solutions of these two salts being somewhat different.

The solutions to be compared must be at the same temperature, and must contain equal amounts of ammonia; they must be prepared

[1] *Cf.* L. F. Clark, *Ind. Eng. Chem.*, 1919, 11, 1138.

with distilled water, quite free from organic matter, and with pure ammonia, otherwise a greenish coloration results. Bituminous ores must be roasted to decompose organic matter before being treated with acids.

Nickel and cobalt interfere with the determination, as also arsenate of iron, which gives a brown coloration with ammonia; small quantities of nickel give the solution a violet tinge which is difficult to compare with the blue of pure copper. These impurities may be removed by previous precipitation of the copper as sulphide, which is then dissolved in nitric acid; it is also advisable to precipitate the copper as sulphide from solutions containing much iron and aluminium, as the bulky precipitates of the hydroxides of these metals retain copper tenaciously.

Heine's Method for Low-grade Ores and Slags.

Solutions of sulphate of copper, containing exactly 1 mg. of copper per cubic centimetre, are made by dissolving electrolytic copper in nitro-sulphuric acid and evaporating down to fumes; quantities of 20, 10, 7·5, 5, 4, 3, 2, 1 c.c. are taken out with pipettes and put into measuring flasks or cylinders; after adding 10 c.c. of pure ammonia to each, they are diluted to 100 c.c. and placed in perfectly similar, square glass-stoppered bottles of about 150 c.c. capacity. The bottles are labelled as 2, 1, 0·75, 0·5, 0·4, 0·3, 0·2, 0·1 per cent.; the stoppers are fastened down with parchment paper caps.

To carry out a determination, 2 g. of an ore is roasted in a porcelain crucible in a muffle and then treated in a beaker with 15 c.c. of a mixture of three parts of sulphuric acid of sp. gr. 1·26, and one part of nitric acid of sp. gr. 1·2, and the whole boiled down on a sand-bath until sulphuric acid fumes are evolved. On cooling, the mass is taken up with distilled water, and the volume made up to 100 c.c. in a graduated flask, 30 c.c. of strong pure ammonia added, and the whole well mixed and filtered into the sample bottle, marked for 200 c.c. After cooling, the solution is diluted to the mark and the bottle placed between the standard bottles, at a window, in front of a screen covered with white paper. If the colour of the ammoniacal solution from 2 g. of ore, diluted to 200 c.c., agrees with the standard solution of 20 mg. of copper in 100 c.c., it follows that the ore contains 2 per cent. of copper; should the colour be deeper than that of the strongest standard, the assay solution is diluted to twice its volume and a sample bottle filled with the diluted solution, comparisons being again made, and so on.

According to Heath,[1] slags at the works at Lake Superior are usually assayed colorimetrically, as follows:—Two and a half grams

[1] *Eng. and Min. J.*, 1895, 59, 369, 370; *J. Soc. Chem. Ind.*, 1895, 14, 679.

of finely powdered slag is boiled in a porcelain dish with concentrated nitric acid (sp. gr. 1·4), until all nitrous fumes are driven off, 10 c.c. of sulphuric acid then added, and the boiling continued until the mass is pasty. After taking up with water and adding excess of ammonia, the solution is filtered on the pump into a 200 c.c. graduated bottle and the precipitate washed with very dilute ammonia (1 to 10); the cooled solution is then made up to 200 c.c. and the test carried out as described above with suitable standards.

J. D. Audley Smith[1] uses only one solution containing 2·5 mg. of copper per cubic centimetre for the comparison. The solution under examination is placed in a 200 c.c. bottle; 150 c.c. of water is placed in a similar bottle, the same amount of nitric acid and of sulphuric acid as the sample, and 30 c.c. of ammonia (sp. gr. 0·9), added, and a copper solution of known strength then run in from a burette until a corresponding colour is produced, when made up to 200 c.c.

Refractory slags are best heated with potassium fluoride and sulphuric acid in a platinum dish, the residue dissolved, the iron oxidised with nitric acid, and the solution then evaporated down until fumes of sulphuric acid are evolved; the colorimetric comparison is then made as above.

For the determination of small quantities of copper in litharge, 10 g. or more of the sample is treated with dilute nitric acid, evaporated down with sulphuric acid, 50 c.c. of water added, and the solution filtered and treated as above.

Waller[2] gives the following method for the colorimetric determination of copper in slags:—Two grams of the slag is placed in a small beaker, 50 c.c. of hot water and then 15 c.c. of hydrochloric acid added at once while the slag is kept in suspension by vigorous stirring. Practically all the silica, lime, oxide of iron, etc., is dissolved, and can be filtered off from the black residue, which consists of copper sulphide and a little partly decomposed slag and matte. The solution always contains sulphuretted hydrogen, which ensures the precipitation of the copper. The residue is filtered off on the pump, as otherwise the filtration is slow owing to a slight separation of gelatinous silica. The filter paper is ignited in a porcelain crucible, the residue brushed into a beaker, 5 c.c. of nitric acid and a few drops of hydrochloric acid added, and heated till red fumes cease to come off. The resulting solution is then diluted, 20 c.c. of ammonia added, the solution boiled, filtered into a colorimetry bottle, cooled, and diluted to 150 c.c. A double precipitation with ammonia is not necessary, as the amount of iron to be separated is very small and does not carry down appreciable amounts of copper. The iron and copper present at this stage are

[1] *Trans. Amer. Inst. Min. Eng.*, Canadian Meeting, 1900; *Chem. Zeit. Rep.*, 1900, **24**, 291.
[2] *Trans. Inst. Min. and Met.*, 1908-9, **18**, 37.

derived chiefly from shots of matte which have been included in the slag. The standard colorimetry bottles are generally made up about once a month; they do not alter appreciably in colour over a much longer period, but the ammonia attacks the glass, forming a flocculent precipitate which, if shaken up in moving the bottles, clouds the solution. The standards are, however, quickly renewed as follows: 0·5 g. of copper is dissolved in a little nitric acid, the red fumes boiled off, and the solution diluted to 500 c.c. Ten colorimetry bottles are taken, labelled 0·1, 0·2, 0·3, etc., 5 c.c. of nitric acid placed in each, then diluted, and from a burette, 1 c.c. of the above solution added to the first, 2 c.c. to the second, and an additional 1 c.c. to each successive bottle. Twenty c.c. of ammonia is then added to the contents of each bottle, after which they are filled with water up to the bottom of the labels, which are placed so that each solution has a volume of 150 c.c. For the colorimetric comparison, the bottles are placed on a level with the eye, on a narrow shelf covered and backed with white paper or tiles; there should be only one source of light, directly behind the observer, and there should be space enough on the shelf between the standard bottles to allow for the introduction of the bottle to be compared, which is moved along until its place in the series is determined. Since 2 g. of slag is taken, the factor on the corresponding bottle, divided by two, gives the percentage of copper in the slag.

D. Analysis of Cupriferous Materials

1. COPPER ORES, MATTES, SPEISSES, AND SLAGS

1. Determination of Copper.

The solution of the very finely powdered substance is effected, in general, as described on p. 169. Bituminous ores are subjected to a preliminary roasting; very arsenical and antimonial ores and speisses are roasted carefully at a gradually increasing temperature. Treatment with nitric acid, aqua regia, or hydrochloric acid and potassium chlorate, is preferably followed by evaporation with an excess of sulphuric acid, so as to precipitate all the lead. The sulphate solution, filtered from lead sulphate, is frequently suitable for the direct gravimetric determination of the copper by electrolysis, and also for titration by one or other of the methods described, but with impure materials a preliminary separation of the copper is necessary (pp. 178 and 182).

Copper Pyrites, which is the most common ore of copper, may be assayed electrolytically, or volumetrically by the methods of Low (p. 182) or Parkes (p. 181).

The copper in pyrites and in burnt pyrites may be determined by Nahnsen's method[1] (*cf.* Vol. I., p. 380).

Slags rich in Iron are decomposed by hydrochloric acid, the residue containing the copper filtered off, ignited, and dissolved in nitric acid, and the copper determined colorimetrically (p. 188).

Refractory Slags are treated with potassium fluoride and sulphuric acid in a platinum dish, as described on p. 189.

Copper Speisses, *Fahl Ores*, etc., are best dissolved, according to Hampe,[2] by warming with a mixture of nitric and tartaric acids (for 1 g. of material, 30 c.c. of nitric acid of sp. gr. 1·2 and 10 g. of tartaric acid), the diluted solution treated for a considerable time at 60° with sulphuretted hydrogen, and the precipitate extracted with hot potassium sulphide solution; the residue is then heated in a porcelain dish with nitric acid, evaporated with excess of sulphuric acid, and the copper in the filtered solution determined either electrolytically or by one of the volumetric methods.[3]

2. Determination of Sulphur.[4]

Three-tenths of a gram of finely powdered copper pyrites, or of ores and mattes free from lead, is introduced into an Erlenmeyer flask, standing in cold water, and fuming nitric acid added in small quantities of 10 to 15 c.c. at a time, the action being allowed to go on for about an hour. The whole is then heated gradually in a water-bath, so that at the end of three hours it has reached a temperature of 70°, and in the course of another hour it is brought up to boiling point. Should particles of free sulphur still be present, the flask is cooled and the treatment with fuming nitric acid repeated. The solution is then evaporated to dryness in a porcelain dish, first without hydrochloric acid and then twice successively with 10 c.c. of pure hydrochloric acid, the residue taken up with dilute hydrochloric acid, filtered, and the boiling dilute solution precipitated with a slight excess of a boiling 10 per cent. solution of barium chloride. $BaSO_4 \times 0{\cdot}1373 = S$.

The following method may be used for ores, mattes, and slags free from lead (Bannister):—Half a gram of the sample is treated with 10 c.c. of nitric acid, and when the first violent action ceases, crystals of potassium chlorate are added until the whole is decomposed. When all action has ceased, the solution is evaporated to dryness, 10 c.c. of hydrochloric acid added, and the whole evaporated to dryness to render the silica insoluble. The residue is then taken up with hydrochloric acid, the solution diluted with hot water, filtered, the filtrate made alkaline with ammonia, about 3 g. of barium chloride added, the solution boiled

[1] *Chem. Zeit.*, 1887, 11, 692. [2] *Ibid.*, 1891, 15, 443.
[3] For other methods see Offerhaus, *Metall. u. Erz.* 1917, 271.
[4] *Cf.* also, Vol. I., pp. 366 *et seq.*, and p. 383.

for a few minutes, then acidified with hydrochloric acid to redissolve the iron, again boiled for a few minutes, and allowed to settle well before filtering. Barium sulphate can in this way be separated in one operation from solutions containing large quantities of iron without contamination with the latter metal, as the iron is thrown out of solution before the precipitation takes place.

Speisses, fahl ores, raw and roasted copper matte and lead matte are, according to Hampe, examined as follows:—One gram of material is mixed with 6 g. of nitre and 5 g. of pure anhydrous sodium carbonate in a platinum crucible, the mixture covered with a little nitre and carefully fused. The melt is extracted with water, the lead precipitated by means of carbon dioxide and filtered off, and the filtrate, after being acidified with hydrochloric acid, evaporated to dryness; the residue is taken up with dilute hydrochloric acid, any silica filtered off, and the sulphur then precipitated in the ordinary way with barium chloride.

3. Determination of Silica.

In the absence of lead the insoluble matter filtered off after decomposition of the ore or slag as described in the determination of sulphur (p. 191), is ignited and weighed as "insoluble matter." For smelter routine work this is usually the only silica determination required, but it is sometimes necessary to determine the true silica content, when the following method may be used:—The insoluble residue is mixed in a platinum crucible with about 2 g. of sodium carbonate and fused over a blowpipe until all action ceases. The subsequent solution may be greatly facilitated as follows:—The contents of the crucible are poured on to its lid, the crucible and lid each being held by a pair of platinum-tipped tongs; both crucible and lid are then placed in a porcelain dish containing about 40 c.c. of cold water. The bulk of the melt which is on the lid readily slides off, while the crucible retains only a thin film which is quickly dissolved out. The dish is heated until all is dissolved or thoroughly disintegrated, when the crucible is removed, the solution acidified with an excess of hydrochloric acid, evaporated to dryness, the residue, after cooling, moistened with 5 c.c. of hydrochloric acid and a few drops of nitric acid, diluted with hot water, filtered, washed, ignited, and weighed.

With materials containing lead, after decomposition by means of nitric acid, sulphuric acid is added and the solution evaporated to fumes, cooled, diluted, and filtered. The residue is washed back into the beaker, and the lead sulphate present is dissolved in hot ammonium acetate solution and filtered off, after which the lead-free residue is ignited and weighed as "insoluble matter" or is treated for the determination of silica by the method given above.

4. Determination of Alumina and Iron.

For the determination of the alumina, 15 c.c. of a saturated solution of microcosmic salt is added to the filtrate from the insoluble matter, to which is added the filtrate from the silica, the total volume of which should be about 100 c.c. The liquid is then carefully neutralised with ammonia until a slight permanent white precipitate is obtained, heated to boiling and acidified with hydrochloric acid until the solution has cleared, care being taken not to have more than 2 c.c. of acid in excess; 25 c.c. of a saturated solution of sodium thiosulphate is then added and 5 c.c. of glacial acetic acid or an equivalent amount of dilute acetic acid. The solution is boiled for ten minutes, when a white precipitate, consisting of aluminium phosphate and sulphur, is obtained, which is easily filtered and washed. The precipitate is ignited very gently at first until the paper and sulphur are burnt off, and is then heated to a bright red heat; it is quite white and should show no signs of fusion. The weight of $AlPO_4$, multiplied by 0·4184, gives the weight of Al_2O_3.

Alumina and iron may also be determined together in the combined filtrate from the insoluble matter and silica as follows:—The iron and alumina are precipitated with ammonia in the presence of ammonium chloride in the usual way and filtered, the precipitate dissolved in hydrochloric acid, and reprecipitated with ammonia, filtered, washed, ignited, and weighed. This represents alumina plus ferric oxide. The ignited precipitate is dissolved in strong hydrochloric acid, reduced with stannous chloride, 20 c.c. of a saturated solution of mercuric chloride added, and the solution titrated with standard potassium bichromate in the usual way. The iron figure obtained is calculated to ferric oxide which is deducted from the weight of the ignited precipitate in order to ascertain the alumina present.

The iron in slags which can be dissolved in hydrochloric acid may be determined directly in the solution after reduction, by means of potassium bichromate.

5. Determination of Lime.

To determine the lime, an excess of ammonium oxalate is added to the filtrate from the iron and alumina, the solution boiled for a few minutes, filtered, washed, ignited and weighed as CaO, or the filter paper and precipitate may be placed in a beaker containing 10 c.c. of sulphuric acid, diluted to 100 c.c., heated to boiling, and titrated with standard potassium permanganate solution in the usual way.

For the determination of lime in slags, the filtrate from the silica is heated nearly to boiling, a decided excess of ammonia added, then solid oxalic acid until the ferric hydroxide has all dissolved; ammonia

is again added until there is a slight permanent precipitate of ferric hydroxide, the solution again cleared by the careful addition of small quantities of oxalic acid, boiled and filtered. The precipitate is treated as above with sulphuric acid and titrated with standard permanganate, containing 5·635 g. per litre; 1 c.c. = 0·005 g. CaO.

2. MARKETABLE COPPER (TOUGH COPPER AND ELECTROLYTIC COPPER)[1]

The commercial analysis of marketable copper is frequently necessary, as even comparatively small amounts of impurities have a considerable effect on the properties of the metal and of its alloys.

The technical analysis is usually confined to the determination of the copper and of the more detrimental impurities, such as bismuth, antimony, and arsenic only, although a complete analysis is sometimes required. The determination of separate constituents is discussed on pp. 201 *et seq.*

Electrolytic copper is almost chemically pure; it usually contains only traces of sulphur, in the form of enclosed sulphate solution, and frequently also bismuth, antimony, arsenic, iron, selenium, and tellurium.

Refined copper usually contains 0·05 to 0·2 per cent. of oxygen (as cuprous oxide); the impurities proper, viz., arsenic, antimony, tin, lead, nickel, cobalt, iron, sulphur, selenium, and tellurium, in the better classes of copper, do not amount to over 0·7 per cent.

Silver is seldom present to a greater extent than 0·03 per cent., and gold occasionally in traces.

1. Complete Analysis.

After the introduction of electrolytic methods for the determination of copper, Hampe, in 1873 (*loc. cit.*), recommended the electrolytic deposition of copper from a solution of 25 to 30 g. of marketable copper, and the determination of the impurities in the solution,[2] from which the whole or most of the copper had been removed; as bismuth is deposited with the copper, the deposited metal must be redissolved, the nitrate solution boiled down with hydrochloric acid, and the bismuth precipitated as oxychloride. In addition to bismuth, small amounts of arsenic and antimony may come down with the copper. Hampe,[3] determined the antimony deposited with the copper, by dissolving the electrolytic deposit and precipitating the copper in the solution as thiocyanate; this method is fully described later on (p. 199).

[1] *Cf.* Fresenius, *Quantitative Analysis*, 7th edition, vol. ii., p. 400; A. Hollard, *Chem. Zeit. Rep.*, 1900, **24**, 146.

[2] *Cf.* W. H. Woodcock, *Analyst*, 1918, **43**, 88.

[3] *Chem. Zeit.*, 1892, **16**, 417; *J. Soc. Chem. Ind.*, 1892, **11**, 695.

On R. Finkener's recommendation, P. Jungfer[1] investigated the method introduced by Flajolot,[2] in which copper is separated from arsenic and antimony by precipitation as cuprous iodide, and, as an outcome of his work, he introduced the following accurate and rapid method of copper analysis:—

(a) Jungfer's Iodide Method.—Most of the copper is precipitated from a slightly acid nitrate or sulphate solution as cuprous iodide, by addition of potassium iodide in presence of sulphuric acid, sulphur dioxide, and a little potassium fluoride, which forms easily soluble antimony-potassium fluoride; the free sulphur dioxide is removed from the filtrate, the copper remaining in solution, together with the arsenic and antimony, and any bismuth and lead, is precipitated with sulphuretted hydrogen, and the copper, bismuth, and lead separated from a strongly ammoniacal solution of the sulphides, after addition of tartaric acid, according to R. Finkener's method,[3] by carefully adding small quantities of weak sulphuretted hydrogen water and warming. Nickel, cobalt, manganese, and iron may be determined in the filtrate from the sulphides. Bismuth comes down principally with the cuprous iodide, and is, therefore, determined in a separate portion by Jungfer's method (p. 199); silver is also determined in a separate portion.

If the copper under examination dissolves in nitric acid without residue, and only arsenic and antimony are to be determined, precipitation may be effected directly in the nitrate solution; otherwise, it is necessary to evaporate with sulphuric acid to precipitate the lead.

To carry out the determination, 10 g. of the copper, in the form of clean chippings or drillings, is dissolved in a large covered procelain dish, in 40 c.c. of pure nitric acid of sp. gr. 1·4, added a little at a time, 10 c.c. of redistilled sulphuric acid, diluted with 10 c.c. of water, is added, the whole evaporated to dryness on a water-bath, and then heated on a sand-bath until sulphur trioxide vapours begin to come off. The cooled mass is dissolved by warming with 150 c.c. of water, and, after standing for several hours in the cold, the lead sulphate, together with any antimonic acid and lead antimoniate, is filtered off on a small filter. The further treatment of the impure lead sulphate is carried out as described below.

The filtrate is transferred to a large beaker, diluted to about 300 c.c., 150 mg. of potassium fluoride free from arsenic added, then 50 c.c. of a pure aqueous solution of sulphur dioxide, followed by the calculated

[1] *Berg u. Hütten. Zeit.*, 1887, **46**, 490; *Z. anal. Chem.*, 1888, **27**, 63; *J. Chem. Soc. Abstr.*, 1888, **54**, 324.

[2] *Annales des Mines*, 1853, p. 641; *J. prakt. Chem.*, 1854, **61**, 105.

[3] *Mitteil. der Kgl. techn. Versuchsanstalten zu Berlin*, 1889, p. 76; *J. Soc. Chem. Ind.*, 1889, **8**, 733.

amount of potassium iodide, dissolved in a little water and added little by little with stirring. Any iodine set free is removed by means of an aqueous solution of sulphur dioxide.

Ten grams of pure copper require 26·2 g. of pure potassium iodide. The copper may be taken at 99 per cent. pure, so that only 26 g. of potassium iodide is added, the cuprous iodide being appreciably soluble in excess of potassium iodide solution.

When the final portions of potassium iodide and sulphurous acid have been added, the mixture is warmed on a boiling water-bath; the dense greyish white precipitate settles in about ten minutes. The supernatant liquid, which is usually colourless, though occasionally of a faint greenish yellow colour, is decanted as completely as possible through a filter paper, the precipitate washed three or four times by decantation with 100 c.c. of hot water containing a little sulphuric acid, the free sulphur dioxide in the combined filtrates oxidised by iodine solution, and then sulphuretted hydrogen passed for a considerable length of time through the warmed liquid.

The sulphide precipitate, which contains arsenic and antimony, the copper not previously precipitated, and any bismuth, is collected on a filter, washed with water containing a little sulphuric acid and sulphuretted hydrogen, and dissolved off the filter with hydrochloric acid and a little potassium chlorate; the solution, after the addition of a few decigrams of tartaric acid and dilution to 50 c.c., is rendered strongly alkaline with ammonia. Copper (and bismuth) are then separated out as sulphides, by Finkener's method, adding small quantities of dilute sulphuretted hydrogen water and warming gently; the precipitate is quickly filtered off and washed with water containing a drop of ammonium sulphide; the filtrate from this precipitate is acidified with dilute sulphuric acid and warmed, and the arsenic and antimony precipitated with sulphuretted hydrogen.

The impure lead sulphate mentioned above is, after drying, removed as far as possible from the filter paper, which is itself destroyed by being treated with concentrated nitric acid in a porcelain crucible, the acid being evaporated off and the residue carefully heated with a little ammonium nitrate; the main bulk of the lead sulphate is mixed with from three to six times its weight of a mixture of equal parts of sulphur and sodium carbonate, placed in a crucible, the cover put on, and the mixture fused at a moderate temperature. The melt is extracted with hot water and the lead sulphide (containing some bismuth and copper) filtered off and washed, first with a dilute potassium sulphide solution, and then with dilute sulphuretted hydrogen water. The impure lead sulphide is converted into sulphate by treatment with nitric acid and evaporation with sulphuric acid, and weighed (*cf.* Lead, p. 226). From the sulphuric acid filtrate any small quantity of bismuth may be

precipitated by neutralising with ammonia, adding a little ammonium carbonate, and warming for some time; the separated basic carbonate is dissolved in a little hydrochloric acid, most of the free acid removed by evaporation and the bismuth precipitated, as oxychloride, by diluting largely with water.

Antimony and sulphur are precipitated from the sulpho-salt solution by adding excess of dilute sulphuric acid and warming; the washed precipitate is treated on the filter paper with hydrochloric acid and a little potassium chlorate.

The mixture of antimony and arsenic sulphides, obtained from the filtrate from the cuprous iodide, is treated similarly. To the combined solutions a little tartaric acid is added, then a good excess of ammonia, magnesia mixture, and one-third the volume of absolute alcohol; the whole is allowed to stand, covered, for forty-eight hours, to enable the magnesium ammonium arsenate to precipitate completely. The precipitate is then filtered off, washed with a mixture of one volume of strong ammonia, three volumes of water, and two volumes of absolute alcohol, and weighed as magnesium pyroarsenate.

The filtrate is gently heated to drive off the alcohol and most of the ammonia, acidified with sulphuric acid, and the antimony precipitated with sulphuretted hydrogen. The precipitate is filtered off and washed with weak sulphuretted hydrogen water. If the precipitate contains apparently only a few milligrams of antimony, it is dissolved on the filter with yellow ammonium sulphide, the solution evaporated to dryness in a porcelain crucible, then oxidised with nitric acid and the antimony weighed as antimony tetroxide, Sb_2O_4 (*cf.* Antimony, p. 284). With larger quantities of antimony sulphide, the precipitate is washed off the filter paper into a porcelain dish, evaporated to dryness on the water-bath, after which the dish is covered and fuming nitric acid run in from a pipette; the antimony sulphide is oxidised to the oxide and sulphuric acid, with practically no separation of sulphur. Meanwhile any antimony sulphide remaining on the filter paper is dissolved in a little ammonium sulphide and the solution evaporated to dryness in a porcelain crucible on the water-bath. The contents of the dish are transferred to this crucible, oxidised with nitric acid, evaporated, the sulphuric acid driven off, and the residue ignited in the open crucible, finally for a couple of minutes over the blowpipe, and weighed as antimony tetroxide.

Nickel, cobalt, iron, and manganese are precipitated together in the filtrate from the sulphide precipitate. The solution is heated to boiling in a large porcelain dish, the sulphuretted hydrogen oxidised with bromine water, and the precipitation then effected with pure sodium or potassium hydroxide, the precipitate filtered off and washed with boiling water; the mixture of hydroxides is then dissolved in hot,

dilute sulphuric acid, with addition of a little aqueous sulphurous acid, the solution evaporated on the water-bath, and finally taken to dryness with a few drops of nitric acid. The residue, which should not smell of acid, is taken up with water, the solution cooled, neutralised with sodium carbonate, a little sodium acetate added (about six times the amount of the presumed iron), and the whole heated to boiling; after five minutes the basic acetate of iron is filtered off, redissolved in a little hydrochloric acid, the solution diluted with water, warmed, nearly neutralised with sodium carbonate, potassium iodide added, and the solution titrated with sodium thiosulphate.[1] Five cubic centimetres of carbon bisulphide should be added, shaken up, and allowed to stand for half an hour before titration with the thiosulphate. The filtrate is concentrated by evaporation, transferred to a weighed platinum crucible of 100 to 150 c.c. capacity, ammonium sulphate and excess of ammonia added, and the nickel and cobalt deposited together electrolytically in the platinum crucible (*cf.* Nickel, p. 322). Any manganese present separates as a brownish black flocculent precipitate of hydrated peroxide, a portion of which is deposited on the anode but can be easily removed. The hydrated manganese peroxide is collected on a small filter paper, washed with hot water, the filter with precipitate incinerated in a crucible, ignited strongly in presence of air, and weighed as Mn_3O_4.

If the copper under investigation contains tin, this is separated as metastannic acid, together with antimonic acid and lead antimoniate, by boiling the diluted nitrate solution; the filtered solution is cooled and treated with potassium iodide, and so on. The dried precipitate is then fused with sodium carbonate and sulphur, the arsenic, antimony, and tin precipitated as sulphides, and dissolved in hydrochloric acid and a little potassium chlorate; this solution is heated gently for some time to remove free chlorine, cooled, treated with a considerable quantity of pure hydrochloric acid of sp. gr. 1·19, and the arsenic precipitated alone, as sulphide, by passing sulphuretted hydrogen for a considerable time (R. Finkener's method). The liquid, after standing for several hours under a bell-jar, must still smell of sulphuretted hydrogen, otherwise more gas must be passed in; the precipitate is filtered off through an asbestos filter and washed, first with strong hydrochloric acid saturated with sulphuretted hydrogen, and finally with pure water. It is then dissolved off the filter with warm ammonia, the solution evaporated in a porcelain dish, and the residue oxidised with fuming nitric acid in a covered dish and evaporated to dryness; the arsenic is then precipitated as ammonium magnesium arsenate.

[1] *Cf.* Pszczolka, *Chem. News*, 1885, **47**, 107; Parthiel, *J. Iron and Steel Inst.*, 1890, **1**, 374; Carnegie, *Chem. News*, 1891, **60**, 87.

The hydrochloric acid filtrate from the arsenic sulphide is diluted largely with water, a portion of the free acid neutralised with ammonia, and the tin and antimony precipitated as sulphides by a current of sulphuretted hydrogen; the precipitated sulphides are dissolved in hydrochloric acid and treated with iron, which precipitates the antimony quantitatively, while the tin remains in solution as stannous chloride. The tin is precipitated in the filtrate from the antimony as dark brown stannous sulphide by means of sulphuretted hydrogen (*cf.* Tin, p. 259).

The noble metals in marketable copper and in blister copper are determined by scorifying with lead, concentrating and cupelling (*cf.* Silver, p. 115), or they may be determined by the Combined Wet and Dry Method described on p. 114.

The determination of bismuth by Jungfer's method (*loc. cit.*) is carried out as follows:—Ten grams of copper is dissolved in about 50 c.c. of nitric acid (sp. gr. 1·4), the clear solution diluted with 100 c.c. of cold water, and dilute sodium carbonate solution added, with stirring, until a slight permanent precipitate is produced; the liquid is then stirred for a few minutes and allowed to stand for one or two hours. The whole of the bismuth is precipitated, and after allowing to settle well is filtered off, washed thoroughly, dissolved in a little hydrochloric acid, most of the free acid evaporated off, and the bismuth precipitated as oxychloride, by dilution with about a litre of water; after standing for from two to three days, the oxychloride is collected on a small filter paper, dried at 110°, and weighed.

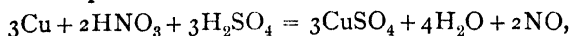
The amount of pure potassium iodide used in this method is considerable; the cuprous iodide is kept, washed by decantation with water, then stirred to a thin paste, and heated with an excess of clean iron turnings; the colourless solution of ferrous iodide is filtered off and the iron precipitated with a sufficiency of pure potassium carbonate, after which the solution of potassium iodide may be evaporated and the potassium iodide crystallised out.

(b) Hampe's Thiocyanate Method.[1]—A sulphate solution of the sample is made and filtered from lead sulphate and insoluble cuprous and bismuth antimoniates, the filtrate collected in a 2-litre flask, sulphur dioxide passed in, and the copper almost completely precipitated in the cold by means of a carefully measured amount of an aqueous solution of pure potassium thiocyanate; a little copper, and the whole of the arsenic, antimony, tin, bismuth, nickel, cobalt, iron, and manganese remain in solution and are estimated by the methods described above (Method (**a**)).

To carry out the determination, 25 g. of copper is dissolved by warming in a large beaker with a mixture of 200 c.c. of water, 100 c.c.

[1] *Chem. Zeit.*, 1893, 17, 1691; *J. Soc. Chem. Ind.*, 1894, 13, 421.

of pure sulphuric acid, and 45 to 46 c.c. of nitric acid (sp. gr. 1·21). According to the equation—

$$3Cu + 2HNO_3 + 3H_2SO_4 = 3CuSO_4 + 4H_2O + 2NO,$$

the amount of nitric acid used is sufficient for the oxidation of the copper, and very little excess remains in the solution. After diluting with 200 c.c. of water, the lead sulphate is filtered off and treated as described above (Method (**a**)). To decompose the nitric acid, sulphur dioxide is passed into the filtrate, warmed to about 40°, so long as red fumes are evolved. Further treatment with sulphur dioxide precipitates metallic silver, and the addition of a few drops of hydrochloric acid precipitates the remainder of the silver as chloride; after standing for twenty-four hours, the silver precipitate is collected on an ash-free filter paper, the paper incinerated, and the silver chloride scorified with a little lead and then cupelled as described on p. 110.

The solution is then transferred to a 2-litre flask, a rapid current of sulphur dioxide passed in, and an aqueous solution of potassium thiocyanate, nearly sufficient for the precipitation of the copper, added little by little; the strength of the potassium thiocyanate solution must have been previously ascertained by standardisation with silver solution (*cf.* Silver, p. 122); 107·88 parts of silver are equivalent to 63·57 parts of copper. About 500 c.c. of the thiocyanate solution should be sufficient for the precipitation of 25 g. of copper. The treatment with sulphur dioxide is discontinued as soon as the liquid, after shaking, smells distinctly of the gas. The delivery tube is then removed, and the flask filled to the mark with water; the liquid cannot be mixed in the flask, on account of the dissolved sulphur dioxide, but must be poured into a large dry beaker and then well mixed by stirring.

When the thiocyanate has settled fairly completely, the greater part of the solution is filtered through a dry pleated filter paper into a large dry beaker, and a measured portion, say exactly 1800 c.c., taken for analysis.

The sulphur dioxide is driven off by heating the liquid, and sulphuretted hydrogen then passed for some time. The filtrate from the sulphide precipitate contains a good deal of free sulphuric acid, as a considerable excess has been used for the solution of the copper to prevent the precipitation of basic salts of bismuth and of antimony during the dilution to 2 litres; before precipitating the nickel, cobalt, iron, and manganese with ammonia and ammonium sulphide, or with sodium hydroxide, the greater portion of this free sulphuric acid should be removed by evaporating down and heating the concentrated solution on a sand-bath. The above metals are then precipitated from the solution after dilution, and their separation effected by the usual methods (*cf.* Method (**a**)). In the analysis of particularly pure brands of copper, 25 c.c. of sulphuric acid will suffice for 25 g. of copper.

For the calculation of the results, the volume occupied by the thiocyanate precipitate produced by 25 g. of copper must be known; according to Hampe, its specific gravity is 2·999. The amount obtained from 25 g. of copper thus occupies 15·983 c.c.; hence, the supernatant liquid in the 2-litre flask occupies 2000 − 15·983 = 1984·017 c.c. Assuming that from 1800 c.c. of filtrate the arsenic obtained was 0·102 g., the amount in the whole 25 g. of copper would be

$$= \frac{0.102 \times 1984.017}{1800} \text{ g.}$$

Copper, oxygen, sulphur, and phosphorus are determined in separate samples. Selenium and tellurium separate with the silver, on passing in sulphur dioxide; they are determined as described on p. 211.

For the determination of the noble metals, *cf.* the sections on Silver and Gold, pp. 115 and 150.

2. Separate Determinations.

The separate determination of the several constituents in marketable copper is much more frequently required than the lengthy complete analysis.

Copper.—Five grams of an average sample is dissolved in 20 c.c. of nitric acid of sp. gr. 1·4, and the solution diluted to 250 c.c.; 50 c.c., corresponding to 1 g. of material, is then taken for the electrolytic deposition of the copper (pp. 170 *et seq.*). This method is extensively used for blister-copper and for marketable copper. The copper in samples of metallic copper free from interfering impurities is frequently determined by the Iodide Method, p. 182. Samples of impure copper, especially when containing bismuth, arsenic, and antimony, should be subjected to a preliminary separation before electrolysis.

Total Oxygen.[1]—(a) *Reduction in Hydrogen.* Ten grams of clean drillings are heated in a hard glass bulb, in a current of pure dry hydrogen, at a dull red heat for about an hour; the time, however, varies according to the size of the drillings;[2] for strips, two hours, for ¼-inch cubes, five hours, are necessary. The narrow end of the bulb-tube should be drawn out to a length of about 20 cm. In samples containing much arsenic and antimony, these constituents volatilise partially and form a mirror-like deposit in the narrow tube. Small quantities of sulphur (probably due to sulphur dioxide, absorbed by the copper) may be evolved in the form of sulphuretted hydrogen, which may be oxidised in a small bulb by means of a mixture of hydrochloric acid and bromine and subsequently determined as barium sulphate.

[1] *Cf.* R. H. Greaves, *J. Inst. Metals*, 1912, **7**, 232; T. West, *J. Inst. Metals*, 1913, **10**, 371.
[2] Archbutt, *Analyst*, 1905, **30**, 385.

The hydrogen is produced in a Kipp generator, from pure zinc and pure dilute sulphuric acid, and is purified and dried by passing through small wash-bottles, containing an alkaline lead solution, silver nitrate solution, and distilled sulphuric acid respectively.

After allowing to cool and displacing the hydrogen by air, the loss of weight is ascertained; this loss, less the sulphur, is equal to the total oxygen. Refined copper contains from 0·05 to 0·2 per cent. of oxygen.

When the copper is comparatively free from arsenic, antimony, and sulphur, the heating in hydrogen may be carried out in a porcelain boat placed in a combustion tube and the water formed during the operation absorbed in suitable weighed tubes and the oxygen calculated from the weight of water obtained. A useful check is obtained by weighing the copper after the operation.

Fig. 46 shows a suitable arrangement of the apparatus in which

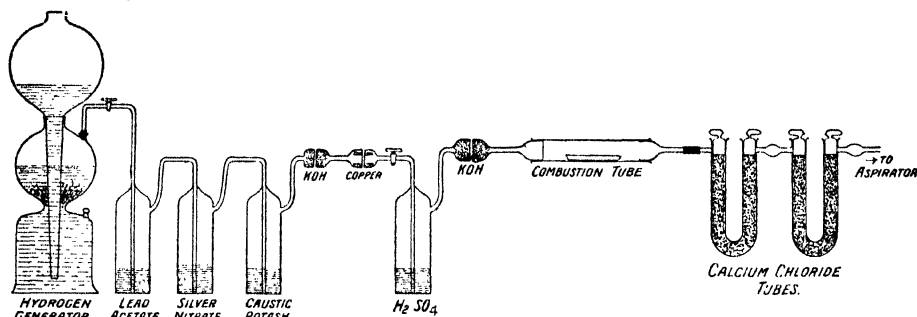



FIG. 46.

hydrogen is generated from pure zinc and dilute sulphuric acid and is purified by passing through a train of wash bottles containing solutions of lead acetate, silver nitrate, and potassium hydroxide, and through a tube containing solid potassium hydroxide. It is next passed through a heated Jena glass tube containing copper gauze, then through sulphuric acid and over solid potassium hydroxide. The gas is next passed over the sample of copper contained in a boat in a silica combustion tube heated in an electric tube furnace, then through a weighed calcium chloride absorption tube, followed by a guard tube and aspirator. All parts of the apparatus should be sealed together or connected together by ground glass joints secured by rubber bands.

In carrying out the determination, 10 g. of the copper drillings are introduced into the combustion tube and the absorption tube, guard tube and aspirator attached. A slow current of hydrogen is passed for half an hour and the absorption tube detached and weighed. The tube is now replaced, the current of hydrogen passed for a quarter of an hour and the reduction commenced by heating the silica tube to 750°,

measured by means of a thermocouple pyrometer. The heating is continued for one hour, then the furnace is allowed to cool whilst the hydrogen is still passed, the absorption tube detached and weighed. The loss in weight of the copper should be ascertained as a check, the boat replaced in the combustion tube and the operation repeated until a constant weight is obtained.

(b) *Reduction in Carbon Monoxide.* E. Murmann[1] first used this gas for reducing oxidised copper; he concluded that to reduce the oxide completely the metal must afterwards be heated in a current of hydrogen. He calculated the oxygen by weighing the copper before and after reduction. M. Lucas[2] also determined the oxygen in copper by fusing the copper with pure tin in a current of carbon monoxide

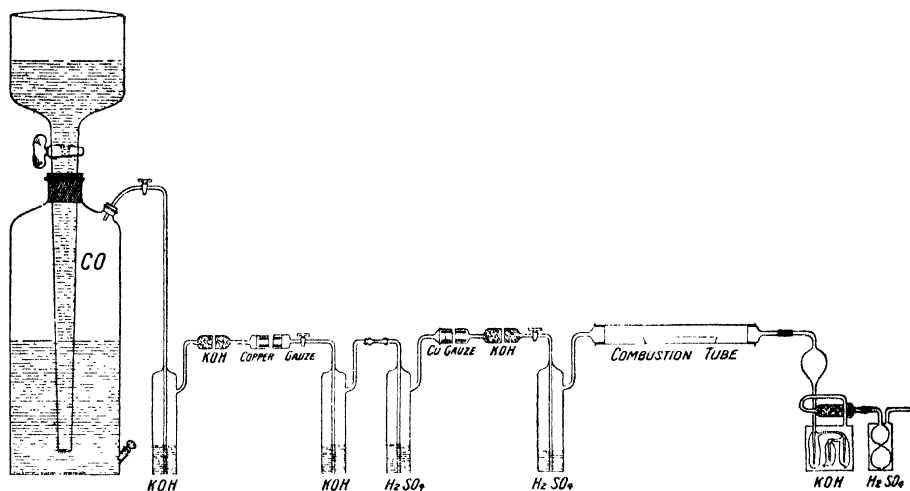



FIG. 47.

and weighing the carbon dioxide formed. He found the results obtained agreed with those determined by ignition in hydrogen. The method, as used by T. West,[3] is carried out as follows:—

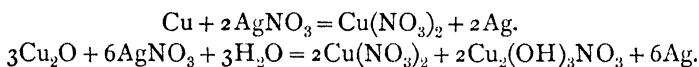
From 5 to 10 g. of the drillings are weighed into a boat and inserted into a silica combustion tube, contained in an electrically heated tube furnace. Carbon monoxide, previously prepared by heating a mixture of sodium formate and sulphuric acid, is passed through a series of purifying and drying tubes as indicated in Fig. 47. This train consists of a solution of potassium hydroxide and solid potassium hydroxide to absorb carbon dioxide, a heated silica tube containing copper gauze to remove oxygen, a solution of potassium hydroxide to absorb any

[1] *Monatsh.*, 1896, **17**, 697.
[2] *Bull. Soc. Chim.*, 1900, **23**, 900.
[3] *Loc. cit.*

carbon dioxide formed, strong sulphuric acid to absorb moisture, another heated tube containing copper gauze followed by solid potassium hydroxide and sulphuric acid. After passing over the copper drillings the gas is passed through the absorption bulb containing potassium hydroxide solution and fitted with a tube containing solid calcium chloride and finally through a guard tube containing sulphuric acid. The carbon monoxide is passed over the copper, heated to about 1000° for one to two hours and the oxygen content calculated from amount of carbon dioxide formed. The process may be modified by mixing with the copper, one-fifth of its weight of pure tin and the combustion may then be carried out at 900°, as at this temperature a molten alloy is formed.

Cuprous Oxide. The cuprous oxide present in copper may be determined by taking advantage of the difference in behaviour of copper and cuprous oxide towards various reagents, especially silver nitrate,[1] dilute hydrochloric acid in the absence of oxygen,[2] or ammonia in the absence of oxygen.[3]

In the silver nitrate method, a suitable quantity of the copper drillings is treated at 0° for 24 or 36 hours with a cold solution of silver nitrate containing less than 60 per cent. of the silver salt; the precipitate obtained consists of a mixture of metallic silver and a basic copper salt according to the following reactions:—

$$Cu + 2AgNO_3 = Cu(NO_3)_2 + 2Ag.$$
$$3Cu_2O + 6AgNO_3 + 3H_2O = 2Cu(NO_3)_2 + 2Cu_2(OH)_3NO_3 + 6Ag.$$

The precipitate is filtered off, thoroughly washed, and the copper determined electrolytically after separation of the silver present, or by some other suitable method, when the resulting figure, multiplied by 1·689, gives the cuprous oxide present.

Sulphur.—The best method for this determination is that proposed by Lobry de Bruyn.[4] Five grams (less in the case of blister-copper) is dissolved in pure nitric acid, the solution diluted, and the copper deposited electrolytically. To remove nitric acid, the solution is heated after the addition of a little sodium carbonate, first over the free flame and finally on a water-bath; the residue, which consists chiefly of ammonium nitrate, is evaporated twice with 50 c.c. of pure hydrochloric acid, then taken up with hydrochloric acid and water, and the boiling solution precipitated with barium chloride solution.

[1] W. Hampe, *Z. anal. Chem.*, 1874, **13**, 215; 1878, **17**, 127. *Berg u. Hütten. Zeit.*, 1897, **56**, 201, 297. Sabatier, *Comptes rend.*, 1897, **124**, 363.
[2] F. Jean, *Ann. Chim. anal.*, 1896, **1**, 185.
[3] G. Coffetti, *Gazz. Chim. Ital.*, 1909, **39**, 137; R. H. Greaves, *Chem. News*, 1909, **100**, 233.
[4] *Rec. Trav. Chim.*, **10**, 125; *Chem. Zeit. Rep.*, 1891, **15**, 354; *J. Chem. Soc. Abstr.*, 1892, **62**, 753.

Sulphur may be determined in the solution obtained by dissolving the copper, without the preliminary removal of this metal, provided the nitric acid is got rid of by evaporating with hydrochloric acid.

Phosphorus.—This element is seldom found in marketable copper and then only in traces. If the copper is free from arsenic, a concentrated solution, containing but little free nitric acid, may be treated directly in the cold with molybdate solution and a considerable quantity of solid ammonium nitrate; the precipitate of ammonium phosphomolybdate is filtered off after standing for twenty-four hours, and the precipitate weighed direct as described on p. 214 or converted into magnesium pyrophosphate by solution in ammonia, precipitation with magnesia mixture and ignition of the filtered precipitate.

When the copper contains arsenic, which is present in most brands, 10 g. is dissolved in just sufficient nitric acid, the solution diluted to 200 c.c. and treated with sodium carbonate, as in the determination of bismuth by Jungfer's method (p. 199); sufficient sodium carbonate is added to the neutralised solution to precipitate about 0·2 g. of copper, The hydrochloric acid solution of the filtered precipitate is treated in a flask with 20 c.c. of aqueous sulphurous acid, boiled until it no longer smells of sulphur dioxide, and diluted; sulphuretted hydrogen is then passed into the warm solution, which precipitates copper, bismuth, lead, and arsenic as sulphides. The filtrate from this precipitate is evaporated, the residue again evaporated with 5 c.c. of nitric acid, taken up with a few drops of nitric acid and a little water, and treated with molybdate solution in the usual way. The phosphoric and arsenic acids are completely precipitated with the copper carbonate; it is best, however, to warm the turbid liquid for several hours in a water-bath with frequent stirring, instead of simply stirring, as recommended by Jungfer.

Arsenic.—This is rapidly determined by E. Fischer's distillation method.[1] The arsenic from 10 g. of copper is first precipitated as basic arsenate, together with copper carbonate, as described above, the precipitate filtered off, dissolved on the filter in a little concentrated hydrochloric acid, and the filter paper washed with concentrated hydrochloric acid; to this solution, contained in a flask of about 300 c.c. capacity, 10 g. of ferrous sulphate and 75 c.c. of pure fuming hydrochloric acid are added. (Instead of the ferrous sulphate, 10 g. of Mohr's salt, or, according to Clark, 5 g. of solid cuprous chloride,[2] may be used.) A white rubber stopper, provided with a tube 3 mm. wide, bent at an angle of 70° and having each limb 10 cm. in length, is fixed into the neck of the flask; the tube is connected, by means of a piece

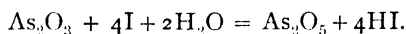
[1] *Ber.*, 1880, 13, 778; *cf.* also, Piloty and Stock, *Ber.*, 1897, 30, 1649; Beck and Fisher, *Chem. News*, 1899, 80, 259.

[2] *Cf.* Vol. I., p. 379.

of strong rubber tubing, with a 50 c.c. pipette, the end of which dips several millimetres below the surface of air-free water, contained in a beaker.

The flask is placed on an asbestos tray, the contents heated to boiling, and the heating continued until about half the liquid has distilled over; the arsenic is thus volatilised as arsenious chloride.[1] The arsenic in the liquid is determined gravimetrically by gently warming, and then precipitating the arsenic as sulphide by means of sulphuretted hydrogen, filtering through a tared filter, drying for three hours at 105° to 110°, and weighing the pure sulphide. $As_2S_3 \times 0{\cdot}6092 = As$.

The following volumetric method is equally accurate. The distillate is neutralised with sodium hydroxide, just acidified with hydrochloric acid, an excess of sodium bicarbonate added, and a little freshly prepared starch solution, and the solution titrated with iodine solution (*cf.* Vol. I., p. 72):—

$$As_2O_3 + 4I + 2H_2O = As_2O_5 + 4HI.$$

In Fischer's distillation method, as later investigations have shown, several distillations are necessary for the complete volatilisation of the arsenic, unless very strong solutions of hydrochloric acid, or the gas itself, are used in the operation. Odling[2] dissolved the copper in ferric chloride and hydrochloric acid, and continued to boil after complete solution had been effected, when the arsenic distilled over as arsenious chloride; to raise the boiling point, which should not exceed 115°, and so ensure the complete volatilisation of the arsenic, T. Gibb[3] added calcium chloride to the hydrochloric acid solution of ferric chloride. A suitable solution is made by dissolving 600 g. of calcium chloride and 300 g. ferric chloride in 600 c.c. hydrochloric acid and making up to 1 litre with water. Beringer[4] found that on boiling a solution of ferric chloride and hydrochloric acid with copper containing 3·48 per cent. of arsenic, only 2·74 per cent. was volatilised by one evaporation; whereas, with the addition of calcium chloride, the whole of the arsenic was volatilised. For the determination, 5 g. of the copper in a finely divided state is taken, 150 c.c. of the solution added to it in a suitable distillation flask, and solution effected by gentle heating followed by distillation, which should be continued until the temperature of the liquid reaches 115°. The distillate is conveniently collected in a three-bulb U-tube containing a little water and kept cool by placing in a beaker of cold water. The arsenic in the distillate is determined by means of dilute iodine

[1] *Cf.* also, the method described on p. 242.

[2] *Chem. News*, 1863, **8**, 27.

[3] *Ibid.*, 1882, **45**, 218.

[4] *Text-book of Assaying*, 15th ed., 1921, p. 385.

solution. (*Cf.* also the following section on the Determination of Antimony.) A blank determination with pure electrolytic copper should be made and an allowance thus made for arsenic in reagents.

Antimony.—The separate determination of antimony is seldom carried out; it may be determined in conjunction with arsenic in the filtrate from cuprous iodide or thiocyanate (*cf.* Complete Analysis, sections (**a**) and (**b**)).

A rapid volumetric method for the determination of antimony and arsenic in copper and cupreous materials generally, is due to Allan Gibb.[1] The ferric chloride and calcium chloride mixture, as used for the distillation of arsenic, solidifies at a temperature which is below that at which antimonious chloride is volatile, but, if the calcium chloride and ferric chloride are replaced by a saturated solution of zinc chloride, a temperature at which antimonious chloride can be volatilised is readily attained; the antimonious chloride is not entirely carried over into the condensing apparatus, a portion of it collecting in the neck of the distillation flask, as practically the whole of the hydrochloric acid is driven off before the antimonious chloride begins to volatilise. It is therefore essential to introduce at this stage some material which shall cause a flow of gas sufficient to carry over the antimonious chloride. The difficulty is surmounted by the introduction of hydrochloric acid when the requisite temperature has been reached. The interval in both time and temperature between the volatilisation of the arsenic and antimony permits each chloride to be collected separately with absolute certainty.

To ensure the reduction of the arsenate and antimoniate, it is well to dissolve part, at least, of the copper in the distillation flask, and it is, therefore, necessary that a reagent capable of bringing the copper rapidly into solution should be added to the acid solution of zinc chloride. Suitable mixtures of zinc and ferric chlorides solidify at temperatures below that necessary for the distillation of antimonious chloride, but a mixture of zinc and cupric chlorides with hydrochloric acid serves well, and such a mixture remains liquid at a temperature considerably over 200°.

The process is carried out as follows:—The weighed sample is dissolved in nitric acid or aqua regia, and the solution, diluted to about 250 c.c., heated nearly to boiling; in the absence of an appreciable amount of iron in the sample, 1 c.c. of a saturated solution of ferric chloride is added, and then solid sodium bicarbonate, until a small permanent precipitate is produced in the hot solution. This precipitate carries down with it all the arsenic and antimony as basic ferric salts. The precipitate is allowed to settle, filtered off through a small filter paper, washed with hot water to remove nitrates, and introduced into

[1] *J. Soc. Chem. Ind.*, 1901, **20**, 185.

the distillation flask with 50 c.c. of the mixture of zinc chloride, cupric chloride, and hydrochloric acid.

This solution is made by mixing a saturated solution of zinc chloride with an equal volume of hydrochloric acid containing 100 g. of copper per litre, in the form of cupric chloride; it should boil at about 108°, and is accordingly concentrated or diluted as required.

About 0·25 g. of pure electrotype copper must be introduced into the flask, together with the precipitate, to reduce the arsenic and antimonic acids, though when the material under examination is metallic copper itself, a portion of the weighed sample may be reserved and used instead, as mentioned above.

The most suitable apparatus for the distillation is an ordinary round-bottomed 250 c.c. fractionating flask, in the neck of which is a rubber stopper provided with two holes, through which pass a thermometer reaching down to within half an inch from the bottom of the flask, and a small tap-funnel containing hydrochloric acid; the stem of this funnel reaches about half-way into the body of the flask, and after being drawn out to a point, is bent so as to carry the cold hydrochloric acid away from the thermometer, and so obviate the danger of cracking the bulb. The end of the delivery tube from the flask is bent and passed through a stopper in one arm of a three-bulb U-tube, standing in cold water, in which the distillate is condensed; the U-tube contains just sufficient water to form a lute. The flask is first heated over wire gauze to gentle ebullition, until the thermometer registers 115°; the whole of the arsenic has by this time come over and the condensing tube is removed and a fresh one attached. It is unnecessary to remove the burner and so cool the flask during this changing of condensers, as no antimony will come over. The wire gauze is then removed and the flask heated over a free flame until the temperature reaches 150° to 160°, which occurs in from ten to fifteen minutes; about 10 c.c. of hydrochloric acid is then run in cautiously from the tap-funnel. As the acid enters the flask, dense white fumes are evolved, and the flow is regulated so that a steady stream of gas passes from the flask; care must be taken that no liquid acid falls on the fused zinc chloride. The heating is continued until the flask is cleared of fumes, when the temperature is usually about 200°; the second distillate is then removed, the fittings of the flask disconnected, and the contents allowed to cool, when the solidified chlorides may be removed with warm water.

The distillates are titrated with iodine solution, made by dissolving 0·85 g. of iodine and 2 g. of potassium iodide in about 25 c.c. of water and making up to a litre; 1 c.c. of this solution is equivalent to 0·00025 g. of arsenic or to 0·0004 g. of antimony. The titration is carried out as follows:—The distillates are washed into separate flasks and a little tartaric acid added to the antimony distillate; the acid solutions are

neutralised with ammonia, slightly acidified with hydrochloric acid, and about 2 g. of sodium bicarbonate added to each. Starch solution is used as indicator, and a blank titration should be carried out on pure electrolytic copper.

Bismuth.—This metal is one of the most detrimental of the impurities in copper, and therefore the accurate determination of small quantities is a matter of considerable importance.

Jungfer's method of determining bismuth has been described above, p. 199. The following method may be employed:—Ten grams of copper is dissolved in a beaker in 60 c.c. of nitric acid (sp. gr. 1·3), any residue being filtered off and fused with sodium carbonate and sulphur, as described under the heading, "Complete Analysis," section (**a**); the clear solution is so far neutralised with pure sodium hydroxide, that a Congo red test paper is rendered only faintly blue, and is then transferred to a 5 litre flask, diluted with 4 litres of distilled water, 5 g. of sodium chloride added, and the whole well shaken. (The sodium chloride keeps the small quantity of silver chloride in solution.) After standing for three days, the precipitate is completely settled, and the clear liquid may be syphoned off and filtered; the precipitate is washed on the filter paper, dissolved in a little hydrochloric acid, the solution made slightly alkaline with ammonia, and the bismuth-iron-antimony precipitate filtered off, washed, and dissolved in a little hot nitric acid of sp. gr. 1·2. Sulphuretted hydrogen is then passed into the diluted solution, and the resulting precipitate is treated on the filter with yellow ammonium sulphide; the bismuth sulphide, which remains behind, is dissolved in hot nitric acid (sp. gr. 1·2), the solution rendered slightly ammoniacal, and the washed bismuth hydroxide precipitate, which is now quite free from sulphuric acid, dissolved off the filter with hot nitric acid, and the solution evaporated in a large porcelain crucible; the residue is heated first on a hot plate or sand bath, then over a free flame, and finally gently ignited and weighed as bismuth oxide. $Bi_2O_3 \times 0{\cdot}8969 = Bi$.

The method of Fernandez-Krug and Hampe[1] is based on that of Fresenius and Haidlen[2] for the separation of copper and bismuth by means of potassium cyanide solution. Ten g. of copper is dissolved in 40 c.c. of nitric acid (sp. gr. 1·4) and the solution evaporated to dryness in a platinum or porcelain dish, on a water-bath, with 20 c.c. of dilute sulphuric acid (1 to 1); the residue is heated on a hot plate, until evolution of sulphuric acid fumes commences, the cooled mass dissolved by warming with 175 c.c. of a mixture of 25 c.c. of dilute sulphuric acid (1 to 1) and 150 c.c. of water, the solution cooled, and the lead sulphate, which is free from bismuth, filtered off.

[1] Private communication to Prof. Pufahl.

[2] Fresenius, *Quantitative Analysis*, 7th ed., vol. ii., p. 403.

The lead sulphate, after being weighed, is examined for antimony by fusing with sodium carbonate and sulphur, and the antimony, if present, determined in the aqueous solution of the melt, as in the complete analysis.

The filtrate from the lead sulphate is treated with 25 c.c. of hydrochloric acid (sp. gr. 1·125), diluted with water to 350 c.c., and a rapid current of sulphuretted hydrogen passed in until the precipitation of the copper is complete; the precipitate is heated nearly to boiling on the water-bath for an hour, the bulky precipitate transferred to an iron-free filter paper and washed well with boiling water. The filtrate must be tested with sulphuretted hydrogen water, to ascertain if any copper remains in solution; after concentrating by evaporation, this filtrate serves for the determination of the iron, nickel, and cobalt. The washed precipitate is transferred to a beaker by means of a bone spatula, and by washing it off the filter paper with a little water; it is then stirred well with solid potassium cyanide until all the copper sulphide is dissolved, giving a pale yellow solution, which is gently warmed and poured through the filter, which still retains a little copper sulphide; if necessary, this residue of copper sulphide must be treated with a little hot potassium cyanide solution. The bismuth sulphide remaining in the beaker and on the filter is washed with hot water, dissolved in warm dilute nitric acid, an excess of ammonia and ammonium sulphide added, and the whole heated for ten minutes in a water bath; the precipitate is then washed, again dissolved in dilute nitric acid, and the bismuth precipitated as hydroxide by means of ammonia, which is added carefully, drop by drop, to slight excess; any traces of copper remain in solution. The bismuth hydroxide is then dissolved in dilute nitric acid, the solution evaporated to dryness in a porcelain crucible, and the residue converted into the oxide by careful heating and ignition, and weighed.

The Colorimetric Determination of Bismuth, as described by C. and J. J. Beringer,[1] is rapid and deserves the special notice of technical chemists. It depends on the solubility of the dark brown bismuth iodide, BiI_3, in potassium iodide solution, and the gauging of the bismuth content of the intense yellow to brownish yellow solution, after dilution to a specified volume, by comparison with standard solutions of known bismuth content, square bottles of the same shape and size being employed.[2] According to Beringer, the nitrate solution from 10 g. of copper is neutralised with sodium carbonate, treated with 1 to 1·5 g. of sodium bicarbonate, boiled for ten minutes, the precipitate filtered off, dissolved in hot dilute sulphuric acid, an excess of sulphur dioxide

[1] *A Text-book of Assaying*, C. and J. J. Beringer, 15th ed., 1921, p. 223. *Cf.* also, The Colorimetric Estimation of Small Quantities of Bismuth, this vol., p. 249.

[2] *Cf.* Heine's Colorimetric Copper Assay, this vol., p. 188.

and of an aqueous solution of potassium iodide added, the whole boiled and filtered, and the filtrate diluted to 500 c.c.; 50 c.c. of the yellow solution are compared with the standard solutions.

Tin.—This seldom occurs as an impurity in copper; it is separated and determined as described under Complete Analysis, section (**a**).

Selenium and Tellurium.—Small quantities of these elements are frequently found in certain brands of marketable copper, and it is possible that the presence of selenium in copper may account for the solution of a small quantity of gold, as it has frequently been noticed that wet methods give lower results than the dry assay for gold in copper.

During the solution of copper for complete analysis by Hampe's method (Complete Analysis, section (**b**), p. 199), selenium goes into solution as selenic acid, H_2SeO_4, and tellurium as tellurious acid, H_2TeO_3; both are precipitated quantitatively by the continued action of sulphur dioxide on the warm solution, the deposit consisting of a dark red or blackish powder of the elements. Selenium gives first an orange-yellow turbidity, and then a red precipitate, which gradually becomes reddish black and at the same time covers the tellurium, which is precipitated simultaneously. Silver comes down at the same time. Should their presence be indicated in this way, the mixture of selenium, tellurium, and silver is treated with nitric acid, the solution evaporated, the silver precipitated by evaporation with a little hydrochloric acid, filtered off, and the selenium and tellurium precipitated together by warming the solution, with repeated additions of sulphurous acid. The precipitate is collected on a tared filter, then dried for four hours at about 110°, and weighed. The filtrate should be tested by warming with sulphurous acid.

Should more than a few milligrams be present, an approximate separation may be effected by H. Rose's method,[1] as follows:—The material is transferred, as completely as possible, from the filter into a Rose's crucible, and the filter paper re-weighed; the mixture of selenium and tellurium is then fused with at least twelve times its weight of potassium cyanide at a moderate temperature for ten minutes in a current of hydrogen, and the melt allowed to cool in hydrogen, extracted with hot water, the dark red solution of potassium telluride diluted considerably, and the tellurium precipitated, as a black crystalline powder, by passing air through the solution for several hours; the precipitate is collected on a tared filter, dried for four hours at 100° to 110°, and weighed. Selenium is estimated by difference.

As a rule, the determination of selenium and tellurium together is sufficient; the total amount of the two in good tough copper rarely

[1] Rose-Finkener, *Handbuch d. analytischen Chemie*, vol. ii., p. 431.

exceeds 0·01 per cent.[1] Tellurium, in presence of seleninm, may be easily detected qualitatively by gently warming a mixture of the two, in a test tube, with 1 or 2 c.c. of concentrated sulphuric acid; according to von Kobell, the tellurium dissolves first, producing a cherry-red coloration; on stronger heating, this coloration disappears and the presence of selenium is then indicated by the yellowish-green colour of the boiling sulphuric acid.

Selenium may be detected also by the characteristic odour produced on burning, and tellurium by the formation of sodium telluride on fusion with sodium carbonate and powdered charcoal; the cooled melt, treated with a little water, gives a purple coloration, which soon becomes turbid with separation of tellurium.

3. BLISTER-COPPER

Blister-copper is always impure, and contains up to 7 per cent. of foreign elements in variable amounts. Iron and sulphur are always present; in addition, the following may occur: lead, arsenic, antimony, bismuth, zinc, nickel, cobalt, tin, gold, silver, platinum, selenium, and tellurium.

As bars are by no means homogeneous, an average sample is best obtained by drilling completely through a considerable number of bars and mixing the fine drillings well together before weighing out.

The analytical examination is conducted essentially as described under Marketable Copper (Complete Analysis, sections (**a**) and (**b**), and also Separate Determinations, pp. 201 *et seq.*). The noble metals are best determined in the dry way by scorification and cupellation, or by the combined wet and dry method (*cf.* Silver, p. 114).

To determine the sulphur, the drillings are dissolved in strong nitric acid, as described under the sulphur estimation in copper pyrites, p. 191; it is to be borne in mind that lead sulphate may be contained in the insoluble residue, which must, therefore, be extracted with ammonium acetate, and the lead reprecipitated with sulphuric acid (or as chromate), and the sulphur in the insoluble matter calculated from this result (*cf.* also p. 204).

4. CEMENT COPPER (COPPER PRECIPITATE)

Copper precipitate, produced from copper liquors and mine liquors, by means of iron (pig iron, scrap, and spongy iron), is usually moist and contaminated by many foreign metals, and also by arsenic, antimony, basic salts of iron, etc.

[1] Egleston found 0·08 per cent. of tellurium in a Colorado copper. As little as 0·03 per cent. in copper produces red-shortness.

Sampling may be effected by taking a considerable quantity from a large number of bags, so that the total amount is, say, 25 kg.; this is dried and sieved through various sized metal sieves, loss through dusting being avoided, so that three or four different products are obtained, portions of each of which are taken, in the ratios of their respective weights, so that ultimately a sample of from 100 to 200 g. is obtained for analysis.

For the analysis, a solution of 100 g. is prepared and diluted to 2 litres; in one portion of the solution copper, bismuth, arsenic, antimony, lead, and iron are determined, according to the methods described for marketable copper; the noble metals are assayed in the dry way.

Moisture is determined on a separate sample of several hundred grams by heating to 100°.

Chlorine is determined by boiling 50 g. with about 300 c.c. of very dilute nitric acid (one volume sp. gr. 1·2 to ten volumes water), filtering, and precipitating a tenth part of the filtrate with silver nitrate.

5. COPPER SCALE, SWEEPINGS, AND RESIDUES

In the absence of dirt, particles of wood, etc., the material is crushed, and a large sample, weighing several kilograms, sieved through various sized metal sieves, and proportional parts are mixed, from which a sample of about 50 g. is weighed out; pieces of iron are removed with a magnet. The remainder is warmed for an hour in a covered porcelain dish on a water-bath with 300 c.c. of ordinary hydrochloric acid, 30 c.c. of nitric acid (sp. gr. 1·2) being added, little by little; as soon as effervescence has ceased, the solution is cooled, diluted, and washed into a litre flask; 50 c.c. is then withdrawn, evaporated down with 5 c.c. of sulphuric acid, the residue taken up with water, a little nitric acid added to the solution, and the copper deposited electrolytically. The filtered sulphate solution may also be precipitated with sodium thiosulphate, and the sulphide dissolved and determined volumetrically.

Clean copper scale may be dissolved in concentrated nitric acid, and the solution, after dilution, electrolysed.

Sweepings containing organic matter are first burnt, then sieved, and, when any amount of metallics is visible, the material is warmed for one or two hours with nitric acid, a little hydrochloric acid being also added. The solution is then diluted considerably, and so much taken as corresponds to from 2 to 2·5 g. of material; this is evaporated with sulphuric acid and treated as usual. Should the material consist almost entirely of oxides, it is dissolved in hydrochloric acid, with the addition of a little nitric acid.

6. PHOSPHOR-COPPER, SILICON-COPPER, AND MANGANESE-COPPER

Phosphor-copper is principally added to bronze alloys as a deoxidising agent, in place of red phosphorus; silicon-copper is used in the manufacture of silicon-bronze (for telegraph wires, etc.); manganese-copper is employed in the manufacture of manganese-bronze. They are made, as a rule, from very pure copper.

All these alloys are brittle and easily powdered; they are analysed in the form of very fine powder.

Phosphor-Copper.—This contains up to 15 per cent. of phosphorus.

Determination of Phosphorus.—Half a gram of the very finely powdered material is heated for a considerable time in a porcelain dish, over a very small flame, with 10 c.c. of nitric acid (sp. gr. 1·4); if, at the end of half an hour, any material is still undissolved, a few drops of hydrochloric acid are gradually added, and the solution obtained is evaporated with 10 c.c. of ordinary nitric acid. (Phosphor-copper dissolves more rapidly in aqua regia, but a considerable amount of phosphorus volatilises as chloride.) The residue from the evaporation is taken up with a little nitric acid and water, any silica filtered off, ammonia added in excess, and the phosphoric acid precipitated with magnesia mixture. Traces of copper in the double salt have practically no influence on the result; the washed ammonium magnesium phosphate may, however, be dissolved in dilute hydrochloric or nitric acid, and reprecipitated pure by the addition of a little magnesia mixture. The precipitate is converted into magnesium pyrophosphate, and weighed. $Mg_2P_2O_7 \times 0{\cdot}2787 = P$.

The phosphoric acid may be precipitated by means of molybdate, in the following manner: One-fifth of the solution of 0·5 g. of material is concentrated to about 10 c.c. by evaporation in a porcelain dish of 250 c.c. capacity, 150 c.c. of molybdate solution, prepared as given below, is added, and as much ammonium nitrate as will dissolve in the cold; the phosphoric acid is precipitated quantitatively, as ammonium phosphomolybdate, in from twelve to eighteen hours. The precipitate is filtered through a hard pressed filter paper with a smooth surface, and is washed with a 20 per cent. solution of ammonium nitrate, containing a little nitric acid; final washings should be given with 5 per cent. nitric acid and water. The molybdate precipitate is dried at 100° to 110°, brushed off the filter paper and weighed, or may be filtered on to a tared filter paper, dried, and weighed. The yellow salt contains 3·753 per cent. of phosphorus pentoxide, or 1·639 per cent. of phosphorus.

The molybdate solution is prepared as follows:—Eighty grams of ammonium molybdate is shaken with 640 c.c. of water and 160 c.c. of ammonia (sp. gr. 0·925) in a flask until dissolved, and this solution

poured in several portions, with continuous stirring, into a well-cooled mixture of 960 c.c. of nitric acid (sp. gr. 1·18) and 240 c.c. of water; the clear solution is syphoned off and kept in a stock bottle, covered with a beaker or other loose cover; if kept in a tightly stoppered bottle, considerable quantities of a yellow acid ammonium molybdate soon begin to separate.

Excess of this solution must be employed for the precipitation, so that not more than two-thirds of the quantity added will be actually required to form the yellow precipitate.

Any arsenic acid in the assay solution comes down in the main as ammonium arsenomolybdate; dissolved silica is also precipitated; both these must, therefore, be removed beforehand (*cf.* Separate Determinations, Phosphorus, p. 205).

Determination of Copper.—One gram of the fine powder is dissolved in a covered porcelain dish by means of a mixture of 10 c.c. of nitric acid (sp. gr. 1·2) and 5 c.c. of ordinary 25 per cent. hydrochloric acid, the solution evaporated down with 1 to 2 c.c. of pure sulphuric acid, 10 c.c. of water added, and the evaporation repeated; the residue is then dissolved in water and electrolysed, after acidifying with nitric acid.

Silicon-Copper.—This may contain up to 50 per cent. of silicon. For the analysis, 1 g. of the finely powdered material is heated for some time in a covered porcelain dish with 10 to 20 c.c. of nitric acid (sp. gr. 1·4), 1 to 2 c.c. of hydrochloric acid added, the mixture again warmed, then evaporated with 2 c.c. of sulphuric acid, and the residue heated until sulphuric acid vapours are given off; the silica is thus rendered insoluble. The residue is taken up with water, the solution warmed, the silica filtered off, washed with hot water, and the copper precipitated from the filtrate. The filter paper with the silica is burnt wet in a platinum crucible and finally ignited strongly. After being weighed, the silica is tested for purity, by dissolving it in 10 c.c. of pure hydrofluoric acid and a drop of sulphuric acid, the solution evaporated, the evaporation repeated with sulphuric acid, and any residue of copper oxide strongly heated in presence of air, and weighed. $SiO_2 \times 0{\cdot}4693 = Si$.

Manganese-Copper.—The manganese content varies, and may be as high as 40 per cent. Sampling is effected by drilling a few ingots and mixing the fine drillings thoroughly. Manganese-copper always contains a little iron (1 to 4 per cent.), a little silicon, and the impurities from the copper used.

The analysis is carried out as follows:—One gram of drillings is dissolved in a covered porcelain dish, in 10 to 15 c.c. of dilute nitric acid, the solution evaporated with 2 c.c. of sulphuric acid, the silica rendered insoluble by further heating, the cooled residue then warmed with sulphuric acid and water, the solution filtered, and the silicon

determined as in the case of silicon-copper; any lead is retained as lead sulphate with the silica, and is dissolved out by treatment with a hot solution of ammonium acetate. The filtrate is diluted to 400 or 500 c.c., a few cubic centimetres of sulphuric acid added, the copper precipitated by passing sulphuretted hydrogen into the warm solution, the precipitate of copper sulphide washed with water containing a little sulphuric acid and sulphuretted hydrogen, and dissolved in nitric acid, and the solution electrolysed (p. 173). The filtrate from the copper sulphide is evaporated in a porcelain dish, and, after the sulphuretted hydrogen has been driven off, oxidised with a few drops of bromine water and concentrated to about 200 c.c.; the cooled solution is made up to 300 c.c. in a graduated flask, and one-third of this taken for the determination of the iron, by reduction with amalgamated zinc and titration with potassium permanganate; the remaining two-thirds is used for the determination of the manganese which is precipitated by adding bromine to excess and then boiling with ammonia, filtering, igniting and weighing as Mn_3O_4, ($Mn_3O_4 \times 0{\cdot}7203 = Mn$) or by titration with permanganate (Volhard's method, pp. 30 *et seq.*).

7. ALLOYS OF COPPER WITH TIN, ZINC, LEAD, IRON, MANGANESE, AND NOBLE METALS[1]

(a) Bronzes.

(Bell metal, gun metal, phosphor-bronze, phosphor-lead bronze, machine brasses, manganese bronze, statuary and medallion bronzes, silicon-bronze.)

One gram of drillings is treated with 10 c.c. of pure nitric acid (sp. gr. 1·4) and 10 c.c. of water in a 250 c.c. beaker covered with a clock-glass. When violent action has ceased, the solution is gently heated, and, after nitrous fumes have disappeared, it is evaporated to a syrup, 100 c.c. of hot water is added carefully, and the whole boiled for five minutes; the metastannic acid is filtered off on a pulp filter, washed with hot 5 per cent. nitric acid followed by hot water, dried, the pulp filter, containing the precipitate, is burnt in a porcelain capsule, and the whole strongly ignited for ten minutes, allowed to cool in a desiccator for half an hour, and weighed. $SnO_2 \times 0{\cdot}7877 = Sn$.

In certain alloys, the metastannic acid is liable to be contaminated with antimony, arsenic, phosphorus, iron, copper, etc., and should be dissolved in hydrochloric acid in the presence of zinc, reduced by gently boiling with iron and titrated with standard iodine (*cf.* Tin, p. 260).

[1] For copper-nickel alloys and German silver, see Nickel, p. 333; for white metals (anti-friction alloys) and britannia metals, see Tin, p. 265; for aluminium bronzes, see Aluminium, p. 316.

The filtrate from the metastannic acid is evaporated on a water-bath in a wide beaker with 2 c.c. of sulphuric acid, the residue dissolved in 30 c.c. of water, the lead sulphate filtered off at the end of an hour on a small filter, washed several times with cold water containing a little sulphuric acid (0·5 c.c. acid to 100 c.c. water), and finally with pure water, then dried, and the paper incinerated at a low temperature in a porcelain crucible; if lead prills are formed, the residue is warmed with a little dilute nitric acid on the water-bath, a drop of sulphuric acid added, the excess of acid evaporated off, and the residue ignited. The larger portion of the lead sulphate is previously transferred from the filter paper to a sheet of glazed paper, and is now added to the contents of the crucible. $PbSO_4 \times 0{\cdot}6832 = Pb$.

The filtrate from the lead sulphate is treated with 5 c.c. of sulphuric acid and 0·2 to 0·5 c.c. of nitric acid (sp. gr. 1·2), and the copper determined electrolytically. In the analysis of ordinary bronzes, the filtrate from the metastannic acid is electrolysed as described under copper and the lead obtained on the anode is weighed as PbO_2 (*cf.* p. 228).

The solution from the deposition of the copper is treated with sulphuretted hydrogen, any copper sulphide filtered off through a small filter, washed with hot water and ignited in air; the small quantity of copper sulphide is converted into the oxide, which is weighed. $CuO \times 0{\cdot}7989 = Cu$.

If the total amount of metals found as copper, tin, and lead amounts to approximately 100 per cent., the filtrate from the copper sulphide may be evaporated and used for the determination of any iron, nickel, manganese, and zinc. The sulphuric acid is evaporated off, without the solution being allowed to boil, and the residue ignited; should this consist merely of a reddish skin of ferric oxide, it is dissolved in hydrochloric acid and again evaporated with a drop of sulphuric acid in a weighed capsule, ignited and weighed as ferric oxide. Zinc, nickel, and manganese may be present in addition to iron; for their determination the residue is dissolved in a few c.c. of hydrochloric acid, evaporated with a few drops of sulphuric acid, the residue taken up with water, and the zinc precipitated as sulphide by means of a current of sulphuretted hydrogen, which is passed for some time through the diluted solution, after neutralising with sodium carbonate (using Congo red paper as indicator), and then slightly acidifying with sulphuric acid (*cf.* Zinc). The filtrate is boiled, excess of bromine water added, and the iron and manganese present precipitated with ammonia; the precipitate is filtered, washed, and ignited; the mixed oxides of iron and manganese are weighed, then dissolved in the smallest possible quantity of hydrochloric acid, 20 c.c. of concentrated ammonium

acetate solution added and sulphuretted hydrogen passed through the solution to precipitate the iron, which is filtered off, ignited and weighed as ferric oxide. This, deducted from the weight of the mixed oxides, gives the weight of Mn_3O_4.

The filtrate from the precipitation of iron and manganese by bromine and ammonia is treated with dimethyl-glyoxime solution and the nickel precipitate is weighed (*cf.* p. 66).

The following rapid method for the analysis of bronzes has been worked out by M. E. Walters and O. L. Affelder[1]:—

One gram of material (or, if the lead content is over 15 per cent., only 0·5 g.) is decomposed by warming with 10 c.c. of nitric acid (sp. gr. 1·42), 40 c.c. of hot water added, and the whole boiled for five minutes. The precipitated oxide of tin is removed by filtration, washed with 2 per cent. nitric acid, ignited, and weighed. To the filtrate 25 c.c. of strong ammonia is added, the solution heated to boiling, then 5 g. of ammonium persulphate added, and the boiling continued for five minutes; after acidifying with sulphuric acid, the precipitated lead peroxide is filtered off, washed with hot water, the precipitate and filter transferred to a beaker, well agitated with 600 to 700 c.c. of cold water, and then about 3 g. of potassium iodide, and starch added. After the potassium iodide has dissolved, 10 c.c. of hydrochloric acid (1 to 1) are added, the whole well stirred and titrated with $N/20$ thiosulphate solution, until the colour changes from dark to very pale yellow; the number of cubic centimetres of thiosulphate solution used, multiplied by 0·5178, gives the percentage of lead. The lead may also be determined gravimetrically.

The filtrate from the lead peroxide is diluted to 500 c.c., heated to boiling, and treated with 50 c.c. of a 20 per cent. sodium thiosulphate solution, for precipitation of the copper; the precipitate is washed with hot water, dissolved, and the copper determined volumetrically. In the filtrate from the copper precipitate, the iron and aluminium are determined as usual, and then the manganese precipitated by boiling the ammoniacal solution with ammonium persulphate.

Excess of ammonium phosphate is added to the filtrate from the manganese precipitate, the liquid heated to boiling, hydrochloric acid added gradually until only a slight smell of ammonia can be detected, the whole then boiled for several minutes, filtered, the precipitate washed with hot water, and then dried at 100° to 105° and weighed as zinc ammonium phosphate, $ZnNH_4PO_4$;[2] or, it may be ignited and weighed as zinc pyrophosphate, $Zn_2P_2O_7$.

Any nickel is precipitated as sulphide in the filtrate from the zinc precipitate. Small quantities of manganese may be determined

[1] *J. Amer. Chem. Soc.*, 1903, **25**, 632; *Z. angew. Chem.*, 1903, **16**, 1081.
[2] *Z. anal. Chem.*, 1900, **39**, 273.

colorimetrically in a separate sample. Phosphorus is precipitated as ferric phosphate in a separate sample, dissolved in nitric acid, lead, tin, and copper being first precipitated by metallic zinc; the phosphorus is then determined in the ferric phosphate by the molybdate method.

Phosphor-Bronze.—The method of analysis is the same as that for ordinary bronze; the phosphorus is determined in a separate portion of the sample as follows:—One gram of fine drillings is treated in a beaker with 10 c.c. of nitric acid (sp. gr. 1·4); after standing for five minutes, the beaker is placed on a hot plate, heated to boiling, at the end of ten minutes the cover-glass removed, and the free acid evaporated off. The residue is stirred with 10 c.c. of hydrochloric acid, again evaporated to dryness, the brown residue dissolved by warming with 10 c.c. of dilute nitric acid, and 50 c.c. of molybdate solution and 15 g. of solid ammonium nitrate added; the whole is well stirred until the ammonium nitrate has dissolved. The yellow precipitate of ammonium phosphomolybdate is filtered off and treated as described under Phosphor-Copper, p. 214.

T. E. Rooney[1] describes a modification of this method in which titration is substituted for the weighing of the precipitate.

Another method, depending on the separation of the phosphorus with the insoluble metastannic acid is frequently used. Five grams of an alloy of low phosphorus content (0·01 per cent.) or 1 g. of a sample containing a higher phosphorus (0·3 to 1·0 per cent.) is decomposed with nitric acid, and the insoluble residue is collected, dried, and ignited in a porcelain crucible. This impure residue is fused with three times its weight of potassium cyanide and the melt, which consists of potassium phosphate, potassium cyanide and cyanate and metallic tin, is extracted with water, separated from metallic tin, acidified with hydrochloric acid, and boiled in a fume chamber until hydrogen cyanide is eliminated. A small quantity of ferric nitrate is added to the solution and then ammonia. The precipitate of ferric phosphate and hydroxide is filtered, washed, and dissolved in nitric acid, and the phosphorus precipitated in the usual way with ammonium molybdate solution.

The above method is somewhat tedious, and the following method, although not so accurate, gives good results. One half to 2 g. of the sample, according to the phosphorus content, is dissolved in 20 c.c. hydrochloric acid with the aid of potassium chlorate. The solution is boiled to get rid of chlorine, diluted with an equal bulk of water, and the copper and tin present are precipitated by pure zinc. The precipitated metals are filtered off and the phosphorus is determined in the filtrate by means of ammonium molybdate.

[1] *J. Inst. Metals*, 1918, **20**, 103.

Silicon-Bronze.—This alloy contains very little silicon, and frequently small quantities of tin and zinc; it is chiefly used in the manufacture of telegraph and telephone wires.

As in the analysis of bronze, 1 g. is decomposed with 10 c.c. of nitric acid (sp. gr. 1·4), 100 c.c. of hot water added, the whole boiled for five minutes, and the siliceous stannic acid filtered off. The filter is incinerated first, then the stannic acid and ash ignited in a platinum crucible and weighed; one drop of sulphuric acid and 2 c.c. of pure hydrofluoric acid are added, the liquid evaporated on the water bath, the sulphuric acid driven off, and the pure stannic oxide weighed after ignition; the loss in weight gives the silica.

For the determination of the dissolved silica, the filtrate from the stannic acid is evaporated to dryness with 3 c.c. of sulphuric acid, the residue heated to drive off this acid, water added, and the silica, which may contain a trace of lead sulphate, filtered off, washed with water treated with a hot dilute solution of ammonium acetate, and a few drops of a solution of potassium chromate added to the filtrate so obtained; any lead chromate precipitated is collected on a tared filter, and dried at 100°. The filter paper with the silica is washed, incinerated and weighed. $SiO_2 \times 0{\cdot}4693 = Si$.

Copper is deposited electrolytically in the filtrate from the silica. The residual solution is then evaporated, sulphuric acid removed by heating, and the iron and zinc determined as described in the section on Analysis of Bronze, p. 217.

If the silicon only is to be determined, the sample may be dissolved in aqua regia, the solution evaporated to dryness, and then again evaporated twice successively with 15 c.c. of hydrochloric acid; the residue is heated to 120°, allowed to cool, moistened with fuming hydrochloric acid, then treated with water and the silica filtered off and washed, etc. After being weighed, it is tested for impurities by evaporation with a little hydrofluoric acid and one drop of sulphuric acid, as above.

(b) Brass and Similar Alloys.

(Brass, yellow metal, tombac, red brass, manganese bronze, Muntz metal, Aich metal, sterro-metal, delta-metal, Dutch metal, bronze powder, hard solder, white brass, button metal, etc.)

These alloys contain copper and zinc as their principal constituents, and either merely the impurities of the copper and zinc, or added tin, iron, manganese, lead, or aluminium.

In the analysis of alloys not containing tin, 1 g. is dissolved in a covered beaker in 10 to 15 c.c. of nitric acid (sp. gr. 1·2), the solution evaporated to dryness with the addition of 5 c.c. of 50 per cent. sulphuric acid, the residue taken up with 30 c.c. of water, cooled, and the lead sulphate collected on a small filter. The copper is deposited electro-

lytically and the solution from the copper determination is neutralised with ammonia in a large beaker; it is then slightly acidified with sulphuric acid, diluted to 400 c.c., sulphuretted hydrogen passed in for two or three hours, and the zinc sulphide filtered off after standing for twelve hours (*cf.* Zinc, p. 293).

The filtrate from the zinc sulphide is evaporated to about 100 c.c., and the iron oxidised with a few drops of bromine water, the excess of bromine boiled off, the cooled solution neutralised, and the iron and aluminium precipitated by ammonium acetate and boiling; the manganese is precipitated in the filtrate in the usual way with bromine and ammonia. The iron and aluminium precipitate is dried, the filter paper burnt in a platinum crucible, the main bulk of the precipitate being added subsequently, and the whole strongly ignited and weighed. (The presence of an appreciable amount of alumina is indicated by a light red colour of the oxides.) The oxides are then fused with six times their weight of acid potassium sulphate, the cooled melt dissolved in dilute hydrochloric acid, and the iron and alumina separated by potassium hydroxide in the usual way (p. 6). $Al_2O_3 \times 0{\cdot}5303 = Al$.

It is much more convenient to determine the alumina in the mixture by difference, by dissolving the melt in the crucible in hot dilute sulphuric acid, washing the solution into an Erlenmeyer flask, then reducing the iron by means of amalgamated zinc and titrating the ferrous sulphate with standard potassium permanganate.

The bismuthate method for the determination of manganese in "manganese bronze" gives satisfactory results. One gram of alloy is treated with nitric acid and tin oxide removed as described on p. 216. Sufficient sodium bismuthate should then be added to the cold solution to oxidise the manganese to permanganic acid, the precipitate filtered off through asbestos and washed with cold 2 per cent. nitric acid until the washings are free from the permanganate colour. The manganese in the solution is determined by titration with a standard solution of ferrous ammonium sulphate.

The following method can be recommended as a satisfactory works' process:—The solution of the alloy and the precipitation of the lead are effected as above; the copper is deposited electrolytically, and then an excess of ammonia added to the residual solution, whereby a yellowish coloration is produced if traces only of iron are present, or a precipitate of ferric hydroxide if there is an appreciable amount, when the iron is subsequently determined volumetrically. The precipitation of the copper may be more rapidly effected (from, say, one-third of the filtrate from the lead sulphate) by means of sodium thiosulphate, after acidifying with sulphuric acid (*cf.* p. 178), and the copper sulphide converted into cupric oxide by roasting. The percentage of zinc is ascertained by difference.

Alloys which contain tin (certain brands of cartridge brass, red brass, bronze powder, hard solder, etc.) are analysed in the same way as bronze.

Even minute quantities of antimony contained in the copper produce cold-shortness in brass, and the resulting alloy is consequently unsuitable for rolling; for this reason electrolytic copper, which frequently contains antimony, is seldom used by brass manufacturers. According to the investigations of E. S. Sperry,[1] best brass for cold rolling should not contain over 0·01 per cent. of antimony. Bismuth is just as injurious; arsenic is less so, in fact, thin sheets are frequently met with, containing as much as 0·1 per cent. of arsenic.

(c) Alloys of Copper with Gold and Silver.

For the determination of the noble metals, *cf.* Gold (pp. 139 *et seq.*) and Silver (pp. 115 *et seq.*).

1. *Gold-Copper Alloys.* The flattened alloy is dissolved in aqua regia, the solution evaporated, and the residue digested with water and a few drops of hydrochloric acid; the resulting solution is diluted and, after standing for several hours, any silver chloride filtered off on a small filter. The gold is precipitated in the filtrate by adding an excess of pure oxalic acid to the hot dilute solution; the carbon dioxide is driven off by boiling, the solution carefully neutralised with pure potassium hydroxide, and the deep blue solution of copper potassium oxalate filtered off; the gold is thus obtained free from copper oxalate. The copper is precipitated by boiling the filtrate from the gold with potassium or sodium hydroxide; the precipitate is filtered off, washed, dried, ignited, and weighed.

If impurities contained in the alloy are to be determined, the gold is precipitated by passing sulphur dioxide into the heated dilute hydrochloric acid filtrate from the silver chloride, the filtrate from the gold boiled to remove sulphur dioxide, then oxidised with a little nitric acid and evaporated with sulphuric acid; any lead sulphate is filtered off and the copper deposited electrolytically and tested for bismuth, which is determined, if present (*cf.* Analysis of Marketable Copper, pp. 194 *et seq.*). The solution from the deposition of the copper is evaporated down, the sulphuric acid driven off, and the iron, nickel, etc., which are present usually in traces, determined in the residue (*cf.* Analysis of Bronze, p. 216).

2. *Silver-Copper Alloys.* (Coinage alloys, silver-plate, silver solder, and bronze powder containing silver, copper, and zinc; coins containing copper, silver, zinc, and nickel, etc.)

[1] *Trans. Amer. Inst. Min. Eng.*, February 1898; *Berg u. Hütten. Zeit.*, 1898, **57**, 117; *J. Soc. Chem. Ind.*, 1898, **17**, 582.

The alloy is dissolved in nitric acid, the solution diluted largely, and the silver precipitated with hydrochloric acid; the filtrate is evaporated to dryness with sulphuric acid, the residue is taken up with water, lead sulphate filtered off, the copper deposited electrolytically and tested for bismuth, and in the residual solution zinc, nickel, and iron determined by the usual methods (*cf.* Analysis of Bronze, pp. 216 *et seq.*).

8. COPPER LIQUORS

From 10 to 50 c.c. of the liquor, according to the content of copper, is evaporated with an excess of sulphuric acid, any lead sulphate that has separated filtered off, and the copper precipitated in the filtrate by pure zinc. The iron is determined at once in the decanted solution by titration with potassium permanganate.

9. COPPER-PLATING BATHS

Fifty c.c. of the solution is evaporated with an excess of sulphuric acid in a fume chamber with an adequate draught to decompose the cyanogen compounds present, and heated until fumes of sulphuric acid are copiously evolved. The residue is allowed to cool, dissolved in water, and the copper determined electrolytically. In most cases it suffices first to decompose the cyanogen compounds, and then to titrate an ammoniacal solution with potassium cyanide (*cf.* p. 181).

LEAD

Until recently, the metal content of ores and of products from lead-smelting works (except in the metal itself and in hard lead) was invariably determined in metallurgical works by quick, dry methods,[1] although such assays gave results from 1·5 to 5 per cent. too low.

On account of the considerable inaccuracy of dry assaying, rapid volumetric methods have been introduced, and are now much used in the laboratories of smelting works and in commercial laboratories.

The products to be examined include: Ores, the products from smelting works (lead matte, lead speiss, litharge, scum, dross, lead fume, slags, work lead, refined lead or commercial lead, hard lead or antimonial lead), lead alloys, scrap lead, etc.

The most important ores of lead are:—

Galena, PbS, containing 86·6 per cent. of lead; it invariably contains

[1] Details on "Lead Assaying" are given by C. and J. Beringer, *Text-book of Assaying*, 15th ed., 1921.

silver as isomorphous Ag_2S, sometimes in quantities over 1 per cent., but most frequently the silver content is from 0·01 to 0·1 per cent.

Cerussite, $PbCO_3$, containing 77·6 per cent. of lead.

Anglesite, $PbSO_4$, containing 68·3 per cent. of lead.

Pyromorphite, or *Green Lead Ore*, $3Pb_3P_2O_8 \cdot PbCl_2$, containing 76·2 per cent. of lead.

The following ores are more rare:—

Mimetite, $3Pb_3As_2O_8 \cdot PbCl_2$.

Crocoisite, $PbCrO_4$; *Wulfenite*, $PbMoO_4$.

Vanadinite, $3Pb_3V_2O_8 \cdot PbCl_2$; *Stolzite*, $PbWO_4$.

I.—Dry Assays for Ores, etc.

Dry assays consist in the separation of the metal by fusion with reducing and fluxing agents; sulphide ores or metallurgical products, when fused in clay crucibles, are desulphurised by addition of metallic iron, or the fusion is carried out in an iron crucible. On account of the volatility of the metal at high temperatures (increased by the presence of arsenic, antimony, and zinc), and to a less extent through scorification, there is always a considerable loss of metal. The lead from impure ores containing antimony, arsenic, copper, zinc, bismuth, etc., is always more or less contaminated by these impurities.

The noble metals are generally determined by special assays (*cf.* Silver, p. 115). They may, however, also be determined by a direct cupellation of the crude lead button, obtained by the "assay in an iron crucible" method (*cf.* Cupellation of Silver, pp. 110 *et seq.*).

1. The Precipitation or Belgian Assay in an Iron Crucible.

This, the best of all dry assays for lead, is specially suited for rich pure galenas. It permits of a larger weight of ore being worked upon than the other assays, and is quick, thereby preventing any great loss of lead. Under the most favourable conditions, a pure galena will yield 85·25 per cent. of lead instead of 86·6 per cent.; the average loss of lead by this assay may be taken at about 2 per cent.

To carry out the determination, a stout iron crucible, about 12 cm. high and 8 cm. in diameter at the top, is heated to a red heat in a wind furnace, the ore and fluxes introduced (*e.g.*, 30 g. ore, 30 g. sodium carbonate, and 3 g. argol; 5 to 10 g. of borax or sodium carbonate may be placed behind this mixture on the metal scoop (Fig. 28, p. 107) and will form a cover to the rest of the charge in the crucible), the crucible is covered and brought to a bright red heat in about ten minutes; within another ten minutes the fluxes become placid and fluid. The crucible is then removed from the furnace, allowed to cool for a few minutes, and the thin fluid contents run into a warm

mould (Fig. 32, p. 109) smeared with black lead. When cold, the slag and lead button are separated by a few blows of a hammer, the button cleaned by washing in hot water and brushing with a stiff brush, then dried and weighed.

Immediately after pouring out the first assay, a further 20 g. of flux mixture is fused in the crucible, and, after heating for about ten minutes, the contents are run into the mould, sometimes yielding another small button of lead; a new assay may then be carried out.

These assays are in use in many lead-smelting works; they are specially adapted to the determination of the content of lead in lead drosses of very varying composition, of which large average samples (after sieving) must be taken.

Any antimony contained in the ore is found nearly quantitatively in the lead button, and may be determined as described under "Hard Lead," p. 238.

2. Other Methods of Assay for Ores containing Sulphur.

Instead of using iron crucibles as in the Belgian method, clay crucibles are frequently used, the iron necessary for the decomposition of the sulphide being provided in the form of an iron rod or as hoop iron. The charge consists of ore 25 g., sodium carbonate 25 g., argol 2 g.; this is placed in a suitable clay pot and covered with a sprinkling of borax. A piece of iron of such length that it allows the crucible to be covered is inserted and the crucible is placed in a moderately hot coke fire, just above a red heat. After the charge is fused and evolution of gas has ceased, the charge is well stirred and the iron removed, precautions being taken to wash off any lead adhering to the iron by means of the slag. The crucible is allowed to remain in the fire for a few minutes longer and then removed, gently tapped and the charge poured into an iron mould. After it is cold, the slag is removed by hammering, the lead shaped into the form of a cube, cleaned, and weighed.

3. Methods of Assay for Oxide Ores and Metallurgical Products.

These substances (*e.g.*, cerussite and litharge) are fused with fluxes and reducing agents in clay pots; in presence of sulphur (*e.g.*, anglesite, scum, lead fume), the addition of iron is necessary, and with a high content of "earths" (*e.g.*, marl in "bottoms"), a liberal addition of borax. For pyromorphite and mixtures containing phosphates, Beringer[1] recommends the following charge:—Ore 20 g., sodium carbonate 25 g., argol 7 g., fluorspar 5 g., 2 g. of borax being used as a cover.

[1] *Text-book of Assaying*, 15th ed., 1921, p. 213.

II.—Wet Assay for Ores, etc.

A. GRAVIMETRIC METHODS

1. Determination of the Lead as Sulphate.

In the assay of ores free from antimony (galena with zinc blende, pyrites, arsenical pyrites, copper pyrites, etc., and gangue) 1 g. of the very finely ground ore is treated in an Erlenmeyer flask with 10 c.c. of nitric acid (sp. gr. 1·4), the contents of the flask shaken round and the latter placed in a slanting position on a hot sand-bath. When the oxidation is complete (after about half an hour), 10 c.c. of 50 per cent. sulphuric acid is added, the contents of the flask mixed and boiled on the sand-bath till sulphuric acid fumes are evolved. To the cooled residue 30 c.c. of water is added, the contents of the flask warmed on a sand-bath for fifteen minutes, cooled, the solution containing the iron, copper, zinc, etc., decanted through a filter paper, the impure lead sulphate washed once by decantation with water acidified with sulphuric acid (0·5 c.c. sulphuric acid in 100 c.c. water) and twice with pure water. Twenty c.c. of concentrated ammonium acetate solution (prepared by neutralising ordinary ammonium hydroxide with 50 per cent. acetic acid), a few drops of ammonia and 20 c.c. of water is next added, and the contents of the flask heated to boiling so as to dissolve the lead sulphate completely. The hot solution is then filtered into a beaker through the paper used for the first decantation, the flask and filter paper washed three times with hot water to which some ammonium acetate has been added, and the lead precipitated again as sulphate in the cooled solution (about 200 c.c.) by the addition of about 10 c.c. of sulphuric acid.

The heavy precipitate is filtered off after standing for one to two hours, washed three times with pure water (the slight solubility of lead sulphate in water may be neglected in this instance), and once with strong alcohol, the paper and precipitate dried in an air-bath, the sulphate removed as completely as possible on to glazed paper, the filter paper ignited at a low temperature in a weighed porcelain capsule, the bulk of the precipitate added, gradually heated to a dull red heat, cooled and weighed. $PbSO_4 \times 0{\cdot}6832 = Pb$.

If small globules of lead or lead sulphide are formed on the ignition of the filter paper, a few drops of dilute nitric acid are added, the crucible warmed on the water bath to assist the reaction, a drop of sulphuric acid added, the excess acid driven off, the bulk of dry lead sulphate added, and the whole treated as above.

It is generally more convenient to collect the lead sulphate on a previously prepared asbestos filter contained in a Gooch crucible, and to wash with dilute sulphuric acid followed by alcohol. After drying,

the crucible and contents are ignited to dull redness in the mouth of a muffle furnace or by placing the Gooch crucible within a larger porcelain crucible and heating the latter over a large Bunsen burner. In some laboratories the Gooch crucibles are not emptied after each determination and successive precipitates are filtered on to the preceding ones. For the assay of ores poor in lead, lead mattes, etc., 5 g. may be taken.

If the ore contains much chalky gangue, a light precipitate of very fine matted needles of calcium sulphate may form over the heavy lead sulphate on cooling the acetate solution to which sulphuric acid has been added. When this occurs the clear solution is decanted as completely as possible from the precipitate, 200 c.c. of water and a few drops of sulphuric acid added, the whole heated for an hour on a hot plate, stirred round frequently, completely cooled, the pure lead sulphate collected on a filter paper and treated as above.

Calcareous ores containing a very small amount of lead are best dissolved in hydrochloric acid, the solution diluted with boiling water (on account of the difficultly soluble lead chloride), filtered into a beaker, the lead, dissolved copper, etc., precipitated by sulphuretted hydrogen, the impure lead sulphide washed off the filter paper, and treated with nitric acid and sulphuric acid as above.

Galena containing antimony is decomposed with strong nitric acid (10 c.c. of sp. gr. 1·4) and 2 g. of tartaric acid in a flask, 50 c.c. of water added, warmed for ten minutes, cooled, and the lead precipitated by the addition of 10 c.c. of sulphuric acid, whereby a small quantity, about 2 mg., remains in solution. After standing for an hour the solution is decanted off, the sulphate washed, dissolved in ammonium acetate and further treated as above. A. H. Low treats galena containing antimony and bismuth with strong nitric acid, boils with sulphuric acid, takes up with water, decants off the sulphuric acid solution, and dissolves the antimony out of the impure lead sulphate by boiling it with a solution of 2 g. of Rochelle salt (potassium sodium tartrate) in 50 c.c. of water to which 1 c.c. of sulphuric acid is added.

Ores rich in antimony (*e.g.*, bournonite, $CuPbSbS_3$) and products from smelting works (lead speisses) are best fused with sodium carbonate and sulphur (or dehydrated sodium thiosulphate), lixiviated with hot water, the insoluble sulphides of lead, copper, iron, etc., collected on a filter paper, washed, transferred from the filter to a dish, treated with nitric acid, and then further with sulphuric acid as above. Antimony and arsenic may be determined in the solution of the sulpho-salts (p. 288). The washed lead sulphate may be quickly and completely converted into carbonate by boiling with sodium carbonate or by digesting with a cold, saturated solution of ammonium carbonate. If the lead carbonate is washed with hot water, dissolved

in dilute nitric acid, the gangue filtered off, and sufficient nitric acid added so that the solution contains fifteen to twenty volumes per cent. of nitric acid of sp. gr. 1·38, a solution is obtained suited to the electrolytic separation of the lead as peroxide (see below). In the filtrate from the lead sulphate (see above) the copper, zinc, iron, etc., may be determined by first precipitating the copper, together with bismuth, arsenic, antimony, etc., by sulphuretted hydrogen.

2. The Determination of the Lead as Metal.

v. Schulz and Low's Method.[1] The lead sulphate from 1 g. of ore (see above), purified by boiling with Rochelle salt solution acidified with dilute sulphuric acid, is dissolved off the filter by a boiling saturated solution of ammonium chloride, after being previously washed with dilute sulphuric acid. The filtrate, after the addition of three small pieces of aluminium foil (1·5 mm. thick, 35 mm. long, and 15 mm. wide), is boiled for five minutes so as to separate the lead as metal. The flask is then filled with cold water, its contents emptied into a large porcelain basin, the lead adhering to the aluminium scraped off under water, the liquid decanted off, and the lead washed into a small porcelain dish. After pouring off the water, the lead is pressed together by means of a small agate pestle, washed several times with distilled water, once with absolute alcohol, then dried quickly in an air-bath and weighed. The total duration of the assay from the decomposition of the ore is forty minutes.

3. Electrolytic Separation of Lead as Peroxide.[2]

On the introduction of electrolytic methods of analysis, C. Luckow found as early as 1865 that lead is separated quantitatively as hydrated peroxide from solutions containing much free nitric acid. This method permits of a separation of lead from copper, gold, mercury, antimony, zinc, cadmium, iron, nickel, cobalt, manganese, and aluminium; silver and bismuth are partially separated as peroxides with the lead. The method is frequently used in conjunction with the electrolytic determination of copper in alloys, the small quantities of lead present being determined on the anodes (*cf.* p. 176).

Details of the apparatus employed in electrolytic analysis are given in Vol. I. (p. 93), and under "Copper," pp. 170 *et seq.*

The solution employed for the electrolysis must be free from chlorine compounds; sulphuric and chromic acids[3] must also be absent

[1] *Chem. News*, 1893, 67, 178.

[2] *Cf.* Literature on Electrolytic Analysis, Vol. I., p. 115; also, H. Nissenson and C. Rüst, *Z. anal. Chem.*, 1893, **32**, 431; Medicus, *Ber.*, 1892, **25**, 2490; *J. Soc. Chem. Ind.*, 1893, **12**, 182; *Chem. Zeit.*, 1895, **19**, 1143; *J. Soc. Chem. Ind.*, 1895, **14**, 1063.

[3] G. Vortmann, *Annalen*, 1907, **351**, 283.

as these lead to high results, while the presence of arsenic, tellurium,[1] or phosphoric leads to low results. By the use of platinum basins sand-blasted or "matted" on the inside, up to 4 g. of peroxide may be firmly deposited; with smooth dishes the deposit easily scales off.

For slow deposition at ordinary temperatures, using a low current density (0·05 ampères per 100 sq. cm.), the solution should contain about 10 per cent. by volume of nitric acid (sp. gr. 1·38), otherwise a separation of metallic lead takes place on the cathode; using a current of $ND_{100}=0{\cdot}5$ ampère, the content of nitric acid should be raised to 20 per cent. by volume.

For more rapid deposition, the method commonly adopted in practical work, a current of 1 to 2 ampères at 2·3 to 2·7 volts is used at ordinary temperatures in a solution containing 20 per cent. by volume of nitric acid (sp. gr. 1·38); at higher temperatures, not above 60° to 70°, 10 per cent. by volume of nitric acid is sufficient. When, on addition of 20 c.c. of water, the freshly wetted surface of the matted dish does not become darkened by further separation of lead peroxide in a quarter or half an hour, the deposition is completed. The current is then switched off, the contents of the dish emptied out, the deposit washed three times with boiling water and once with absolute alcohol, dried in an air bath at 200° for half an hour, and weighed, after allowing to cool for half an hour. The lead peroxide is quickly dissolved off the platinum dish by means of hot, very dilute nitric acid, with addition of small quantities of oxalic acid.

A micro-burner may be advantageously used for warming the dish (to 50° to 60°), a piece of asbestos paper being placed under the dish so as to distribute the heat evenly. The washings must be carefully decanted in case any lead peroxide becomes detached on washing the dish. The drying must be done at 200°, otherwise a small amount of water is retained by the deposit. When properly carried out, the method gives very accurate results.

Rotating electrodes (*cf.* Vol. I., p. 102) may be used to hasten the precipitation of the lead peroxide. F. Exner[2] adds 20 c.c. of concentrated nitric acid to the lead nitrate solution, giving a total volume of 125 c.c., and uses a current of 10 ampères at 4·5 volts, with a cathode rotating at 600 revolutions per minute. The deposit has a uniform velvety black colour; the time required for the deposition is from ten to fifteen minutes. R. O. Smith[3] effects the deposition on a rotating spiral which makes 800 revolutions per minute. A nitric acid solution is used, containing 25 c.c. of nitric acid of sp. gr. 1·4

[1] E. List, *Chem. and Met. Eng.*, 1912, **10**, 135.
[2] *J. Amer. Chem. Soc.*, 1903, **25**, 904.
[3] *J. Amer. Chem. Soc.*, 1905, **27**, 1287.

in 125 c.c. of solution, which is electrolysed at 95°, with a current of 10 to 11 ampères per 100 sq. cm. at 3·6 to 3·8 volts; up to 0·58 g. of lead can be precipitated in fifteen minutes.

H. J. S. Sand[1] has studied the behaviour of lead peroxide deposits on drying and the effect of varying conditions. His results show that too much nitric acid should be avoided, that it is specially important to remove any oxides of nitrogen that may be present by evaporating the solution to be electrolysed to dryness before a determination, and that the temperature should be kept below 97°. The deposited peroxide should be dried in an atmosphere free from moisture, preferably by washing with alcohol and ether in the usual way, and drying over a Bunsen burner, as it is capable of absorbing moisture at about 200°.

As the deposit is usually impure, Hollard and others recommend the factor 0·853 instead of the theoretical 0·866 for calculating the result. R. C. Benner[2] prefers to ignite the peroxide when it is deposited on the inside of a platinum dish, thus converting it into litharge, in which form it may be weighed without error. When the deposition is made on a gauze electrode, however, it is impossible to ignite over a Bunsen burner, as some of the litharge produced is subsequently volatilised or some of the peroxide remains undecomposed giving low or high results respectively. This may be obviated by igniting the gauze electrode in a muffle at a temperature below 500°.

D. A. MacInnes and E. B. Townsend[3] determine the lead by solution of the deposited peroxide in oxalic acid and titration of the excess acid with potassium permanganate.

B. VOLUMETRIC METHODS

1. Alexander's Molybdate Method.[4]

This method is based on the precipitation of lead in hot acetate solution by means of ammonium molybdate, forming lead molybdate, which is insoluble in acetic acid. Excess of ammonium molybdate is recognised by the yellow coloration given to a freshly prepared tannin solution, a drop of the titrated solution being added to a drop of the tannin solution on a pitted porcelain plate. The ammonium molybdate solution is prepared by dissolving 9 g. of the commercial salt in water, adding a few drops of ammonium hydroxide, and diluting to 1 litre. For its standardisation, 300 mg. of lead sulphate is dissolved by warming with a sufficient quantity of dilute ammonium acetate solution, the solution acidified with acetic acid, diluted to 250 c.c.,

[1] *Trans. Faraday Soc.*, 1910, p. 207; *J. Soc. Chem. Ind.*, 1910, **29**, 47.
[2] *Chem. and Met. Eng.*, 1911, **9**, 141; see also C. P. Karr, *Metal Industry*, 1911, **3**, 16.
[3] *Ind. Eng. Chem.*, 1922, **14**, 420.
[4] *Eng. and Min. J.*, 1893, **55**, 298; *J. Chem. Soc. Abstr.*, 1893, **64**, 599.

heated to boiling, and titrated with the ammonium molybdate solution till all the lead is precipitated as the heavy white molybdate. Drops of the tannin solution (0·3 per cent.) are placed on the pitted porcelain plate, and a drop of the solution which is being titrated is added from time to time until a yellow-brown coloration is produced (300 mg. of $PbSO_4$ contain 204·97 mg. of Pb).

The method is carried out at Broken Hill as follows:—One gram of ore is treated in an Erlenmeyer flask with 15 c.c. of strong nitric acid, 10 c.c. of sulphuric acid is added, and the solution boiled till sulphuric fumes are copiously evolved. On cooling, the sulphate is warmed with water, cooled, washed by decantation, first with water acidulated with sulphuric acid, finally with pure water, the decantation washings filtered, the filter paper brought into the flask, 25 c.c. of concentrated ammonium acetate solution added, the solution heated, diluted with 100 c.c. of hot water, and boiled till the lead sulphate has completely dissolved. The solution is then diluted to 250 c.c. with boiling water, and titrated as above. With ores containing over 30 per cent. of lead, 0·5 g. is taken for the determination. The time required is one hour.

The same quantity of ammonium acetate of good quality or made by the neutralisation of ammonium hydroxide (0·880) by addition of acetic acid should be used in each assay, and calcium [1] should be absent.

2. Beebe's Potassium Ferrocyanide Method.[2]

A lead acetate solution, acidified with acetic acid, free from alkali salts, is titrated at the ordinary temperature with a 1 per cent. potassium ferrocyanide solution till a drop gives a brown coloration on a porcelain plate with concentrated uranium acetate solution slightly acidified with acetic acid. The ferrocyanide solution is standardised against a lead acetate solution of known strength.

The impure lead sulphate first obtained from the ore, as described above (pp. 226 *et seq.*), is boiled with Rochelle salt solution, acidified with sulphuric acid, as recommended by A. H. Low (p. 227), for the removal of bismuth and antimony. By digesting the washed sulphate with ammonium carbonate, it is converted into lead carbonate, which is well washed with hot water, dissolved in a beaker in hot dilute acetic acid, and the cooled solution titrated with potassium ferrocyanide.

According to Low, a high content of calcium compounds (up to 30 per cent. of calcium oxide) does not seriously affect the accuracy of the determination, provided the calcium sulphate is completely converted into the carbonate; otherwise, lead is precipitated as sulphate on dissolving the carbonate in acetic acid.

[1] *Cf.* Bannister and M'Namara, *Analyst*, 1912, **37**, 242.
[2] *Chem. News*, 1896, **73**, 18; *Z. anal. Chem.*, 1897, **36**, 58.

3. The Bichromate Method.

The bichromate method is usually carried out as a direct process, but it may also be used indirectly. In both modifications success depends on the quantitative precipitation of lead chromate during titration of a solution of lead acetate with a standard solution of potassium bichromate. The lead solution is prepared as described under (1) p. 230, and is titrated at a temperature near the boiling point.

In the direct method, the precipitate formed during the titration is allowed to settle from time to time, a drop of the clear supernatant liquid is withdrawn and tested on a spot plate with silver nitrate solution until a purple coloration is observed.

In the indirect method, a known excess of potassium bichromate is added to the almost boiling lead acetate solution, the precipitate is allowed to settle after which it is filtered off and washed, and the excess of bichromate titrated with a standard solution of ferrous sulphate.

III.—Analysis of Commercial Lead (Soft Lead, Refined Lead)[1]

Refined lead contains 99·96 to 99·99 per cent. of lead and minute quantities of silver, copper, bismuth, cadmium, arsenic, antimony, iron, nickel, cobalt, zinc, and manganese.

There are several methods used for determining the quality of lead to be used in chemical plant,[2] the most important of which is that employed for the determination of the temperature at which gas is first evolved and at which disintegration takes place on heating lead in concentrated sulphuric acid.[3] Using pure sulphuric acid (96 per cent.), a good chemical lead evolves gas at 190° to 200° and disintegrates at 300° to 312°.

For analysis, bright turnings (a few from as many ingots as possible) or bright scrapings are warmed for a short time with dilute hydrochloric acid, washed with water, and dried quickly. Two hundred grams is weighed out and dissolved in a covered 1500 c.c. beaker by gently warming with 500 c.c. of nitric acid of sp. gr. 1·2 and 500 c.c. of water. The solution is left to stand for twelve hours.

The purer varieties of soft lead give a perfectly clear solution. Any precipitate of lead antimoniate, etc., formed on solution or on standing is filtered off; its further treatment is described below.

The clear or filtered solution and washings is treated in a beaker with 62 to 63 c.c. of pure sulphuric acid, and well stirred during the mixing of

[1] Fresenius' Method modified by Fernandez-Krug and Hampe. *Cf.* A. J. Hemingway, *Proc. Austr. Inst. Min. and Met.*, 1922, **47**, 245.

[2] For details see *Raw Materials for the Manufacture of Sulphuric Acid, etc.*, W. Wyld, pp. 224-239.

[3] D. W. Jones, *J. Soc. Chem. Ind.*, 1920, **39**, 221T.

the two solutions. When cold, the clear supernatant liquid is syphoned off into a large beaker, 200 c.c. of water, acidified with nitric acid, poured on to the lead sulphate, the mixture well stirred with a thick glass rod, allowed to settle, decanted, and this repeated two to three times with 200 c.c. of acidified water, so as to extract the last trace of dissolved foreign metals out of the precipitate.

The combined washings, together with the syphoned solution, are saturated with ammonia in a beaker, 25 to 50 c.c. of ammonium sulphide added, and the whole warmed on a water bath for two to three hours. The precipitate, which contains considerable quantities of lead sulphide, as well as the sulphides of the foreign metals, is filtered off, washed into a large porcelain crucible, and dried. Meanwhile, the residue from the solution of the 200 g. of lead (see above) is dissolved off the filter paper in hydrochloric acid, some tartaric acid and water added, sulphuretted hydrogen passed through, the precipitate containing lead and antimony filtered off, washed into the porcelain crucible, containing the first sulphide precipitate, again dried, and the contents fused with six times its weight of the usual mixture of equal parts of sodium carbonate and sulphur.

The solution obtained on lixiviating the fused mass with hot water is added to the filtrate from the precipitation with ammonium sulphide, acetic acid added till acid, which precipitates the sulphides of arsenic and antimony, together with much sulphur, and then heated for three to four hours on a steam-bath. The precipitate is filtered off, washed with dilute sulphuretted hydrogen water, acidified with a little acetic acid, dried, the free sulphur extracted with carbon bisulphide, the sulphides dissolved in hydrochloric acid and potassium chlorate, and the undissolved sulphur filtered off; a very small filter paper is used for the filtration, and the washing is done with a pipette. The filtrate, after the addition of 0·5 g. of tartaric acid, is neutralised with ammonia, and finally treated with 10 c.c. of strong ammonia (sp. gr. 0·91) and 1 to 2 c.c. of magnesia mixture. After twenty-four hours the magnesium ammonium arsenate is filtered off on to a small paper and washed with dilute ammonia (one volume of sp. gr. 0·91 to two volumes of water). Ammonium sulphide is added to the filtrate and washings, the solution warmed, the antimony precipitated as sulphide by adding excess of dilute sulphuric acid, the precipitate filtered off on to a small paper, dissolved in warm ammonium sulphide, the solution evaporated in a weighed porcelain crucible, the residue oxidised with strong nitric acid, evaporated, the sulphuric acid driven off, the residue strongly ignited, and weighed as antimony tetroxide. $Sb_2O_4 \times 0{\cdot}7920 = Sb$.

The previously obtained precipitate of magnesium ammonium arsenate is converted into pyroarsenate (*cf.* Arsenic Determination in Commercial Copper, p. 205) and weighed. $Mg_2As_2O_7 \times 0{\cdot}4827 = As$.

The residue from the lixiviation of the melt of the ammonium sulphide precipitate with sodium carbonate and sulphur contains lead, copper, silver, bismuth, cadmium, zinc, iron, nickel, cobalt, and manganese, as sulphides. For their oxidation by heating with dilute nitric acid (one volume acid of sp. gr. 1·2 to two volumes water), the small filter paper is spread out in a porcelain dish, the acid poured on, and then covered with a clock-glass. After filtration and washing, the lead is separated by evaporation with sulphuric acid, and the residue of lead sulphate taken up with a little water and filtered off. A considerable excess of sulphuric acid must be used, otherwise some bismuth may be retained by the lead sulphate; recent analyses show that soft leads containing considerable amounts of bismuth occur in commerce.

The filtrate from the lead sulphate is treated with saturated sulphuretted hydrogen water, sulphuretted hydrogen passed in, and the solution gently warmed for some time; copper, bismuth, silver, and cadmium are precipitated and collected on a small filter paper, the filtrate containing iron, zinc, nickel, etc., being set on one side for the time being.

The precipitate is oxidised as before with dilute nitric acid, the nitric acid driven off by evaporating with a few drops of sulphuric acid, the residue taken up with a little water, nearly neutralised with pure sodium hydroxide (from metal), then sodium carbonate and some pure potassium cyanide added, and the solution gently warmed. A precipitate of bismuth is thus obtained which is filtered off, washed, dissolved in a small quantity of nitric acid, reprecipitated with a slight excess of ammonia, filtered off, dissolved in nitric acid, the solution (now free from sulphuric acid) evaporated in a weighed porcelain crucible, the residue heated to a dull red heat, and weighed as bismuth oxide (*cf.* Bismuth Determination in Commercial Copper, p. 209), $Bi_2O_3 \times 0{\cdot}8969 = Bi$.

The filtrate containing potassium cyanide from the bismuth precipitate is treated with a further quantity of cyanide and then a few drops of potassium sulphide solution. A precipitate of silver sulphide and cadmium sulphide may be formed, which is filtered off and dissolved in hot dilute nitric acid. The silver is precipitated by the addition of a few drops of hydrochloric acid and the silver chloride filtered off. The filtrate is evaporated to dryness, any cadmium precipitated by boiling with sodium carbonate, the precipitate collected on a small filter paper, washed with hot water, dissolved in a few drops of nitric acid, the solution evaporated in a weighed porcelain crucible, and the residue converted into cadmium oxide by carefully heating to a red heat. Cadmium is but seldom found in commercial lead, and then only in traces. $CdO \times 0{\cdot}8754 = Cd$.

The filtrate from the silver and cadmium sulphides is evaporated to dryness after the addition of some sulphuric, nitric, and a few drops of hydrochloric acid. The residue is taken up with water, the solution filtered if necessary, the copper precipitated by passing sulphuretted hydrogen, and determined colorimetrically.

The solution containing the zinc, iron, nickel, etc. (see above), is made slightly alkaline in a flat-bottomed flask, ammonium sulphide added, and the contents diluted so as to fill the flask up to the neck, the flask corked and allowed to stand for twenty-four hours or longer. The precipitate is not filtered off until it has completely settled. The filtrate, which may contain some nickel in solution, is acidified with acetic acid, ammonium acetate added, warmed for a few hours, and the sulphur and nickel sulphide filtered off.

The precipitate from the ammonium sulphide is treated on the filter paper immediately after filtration with a solution of six parts of saturated sulphuretted hydrogen water and one part of hydrochloric acid of sp. gr. 1·12, the liquid that runs through being again brought on to the filter paper by means of a pipette. Zinc sulphide and iron sulphide are dissolved, while nickel and cobalt sulphides remain on the paper. After drying this small filter, it is ignited, together with that on which the nickel sulphide containing sulphur was collected, in a porcelain crucible, the residue warmed with a few drops of aqua regia, the solution evaporated completely to dryness, a little ammonia and ammonium carbonate solution added, filtered, boiled in a platinum dish with potassium hydroxide till all the ammonia is driven off, the small amount of precipitate collected on a small filter paper, washed, dried, ignited, and weighed as nickel oxide. $NiO \times 0{\cdot}7858 = Ni$. If desired the nickel may be determined by dimethylglyoxime (factor 0·2031).

After weighing, the oxide is tested qualitatively for cobalt by the borax bead.

The solution containing zinc, iron, and manganese obtained on treating the ammonium sulphide precipitate with sulphuretted hydrogen water and dilute hydrochloric acid is evaporated, oxidised with a drop of nitric acid, precipitated with ammonia, the precipitate filtered off, redissolved in hydrochloric acid, precipitated again with ammonia, washed, dried, ignited, and the iron oxide obtained weighed.[1] $Fe_2O_3 \times 0{\cdot}6994 = Fe$.

As a check it can be dissolved by warming with a little hydrochloric acid, the diluted solution warmed to 70° with potassium iodide, cooled, and the free iodine titrated with sodium thiosulphate in presence of starch solution.

The ammoniacal filtrate from the ferric hydroxide is treated with

[1] For the determination of small quantities of copper and iron in lead, *cf.* C. R. Hardy, *Chem. News*, 1920, **120**, 256.

ammonium sulphide and gently warmed for at least twenty-four hours. Any precipitate that separates is filtered off, washed, and immediately treated on the filter paper with dilute acetic acid so as to dissolve any manganese sulphide mixed with the zinc sulphide. The trace of zinc sulphide is dissolved off the paper in a little hydrochloric acid, the solution evaporated to dryness in a small weighed platinum dish, some moist precipitated mercuric oxide (which must volatilise without leaving any weighable residue) added, the whole evaporated to dryness, gradually heated to a bright red heat, and the residue of zinc oxide weighed (Volhard's method). $ZnO \times 0{\cdot}8034 = Zn$.

The acetic acid solution is evaporated, any manganese precipitated with potassium hydroxide, the precipitate filtered off, the filter paper washed, dried, ignited, the residue ignited with good access of air and weighed. $Mn_3O_4 \times 0{\cdot}7203 = Mn$.

Sulphur in refined lead is determined on a separate portion of the sample,[1] 500 g. of the metal being added slowly to 40 g. of sodium hydroxide fused in a capacious iron crucible; the mixture is heated for fifteen minutes and stirred vigorously with an iron rod.

After cooling the mass is leached with hot water and the filtered solution treated with 20 c.c. bromine water, acidified with hydrochloric acid, and barium chloride solution added, after which the precipitated barium sulphate is treated in the usual way.

Where great accuracy is required a "blank" determination must be carried out and the weight of barium sulphate obtained therefrom deducted from the amount above.

The silver in refined lead is nearly always determined by cupellation (*cf.* "Silver," p. 110), specially large cupels being used each capable of taking a charge of 100 g.

Remarks.—On account of the impurities in soft lead being present in extremely minute quantities, its analysis is most difficult and demands much practical experience. The acids and other reagents used must be carefully tested for impurities, and the filter papers must be free from iron.

IV.—Analysis of Hard Lead (Antimonial Lead)

Hard lead is manufactured in metallurgical works with a high content of antimony (up to 28 per cent.); a sample of 1 to 2·5 g. is sufficient for the determination of the antimony and impurities (copper, arsenic, and frequently tin).

Nissenson and Neumann[2] dissolve 2·5 g. of metal in a 250 c.c. flask

[1] A. J. Hemingway, *Proc. Austr. Inst. Min. and Met.*, 1922, 47, 245.
[2] *Chem. Zeit.*, 1895, 19, 1142. *J. Soc. Chem. Ind.*, 1895, 14, 1063.

by warming with a mixture of 4 c.c. of nitric acid (sp. gr. 1·4), 15 c.c. of water and 10 g. of tartaric acid; after cooling, 4 c.c. of concentrated sulphuric acid is added, the solution diluted, cooled, and made up to the mark; the lead is thus completely precipitated as sulphate. The solution is filtered through a dry paper, 50 c.c. of the filtrate (corresponding to 0·5 g. of metal) made strongly alkaline with sodium hydroxide, 50 c.c. of a cold saturated solution of pure sodium sulphide added, the solution boiled, filtered, the residue washed, and the solution heated to about 80° and electrolysed in a matted dish for the determination of antimony (p. 284).

For the determination of the copper, the precipitate (copper sulphide) formed on warming with sodium sulphide is dissolved in nitric acid, the solution filtered, and the copper determined electrolytically; or if only a small amount is present, it may be determined colorimetrically (p. 187).

If the hard lead contains tin, the solution from which the antimony has been deposited, together with the washings, is evaporated to 150 c.c., and the tin is precipitated as sulphide by acidifying with dilute sulphuric acid. The precipitate is filtered off, dried, and, by very careful heating and final strong ignition with addition of ammonium carbonate in a porcelain crucible, converted into stannic oxide, which is weighed.

If the hard lead contains tin and arsenic, these are best separated by F. W. Clarke's[1] method.

W. Witter effects the separation as follows:—Fifty c.c. of the filtrate from the lead sulphate (see above), corresponding to 0·5 g. of metal, is made alkaline with ammonia, just acidified with hydrochloric acid, 30 g. of oxalic acid added, and sulphuretted hydrogen passed through the boiling solution for twenty minutes. Antimony, arsenic, and copper are precipitated, the small amount of tin remaining in solution. The solution is filtered hot, made slightly ammoniacal, sufficient ammonium sulphide is added to redissolve the precipitate at first formed, then the liquid is acidified with acetic acid; the precipitate (tin sulphide and sulphur) is allowed to settle, filtered off, and converted into oxide as above

The arsenic is extracted from the antimony-arsenic precipitate with ammonium carbonate solution, reprecipitated by acidifying with hydrochloric acid, and finally weighed as magnesium pyroarsenate (*cf.* Arsenic, p. 274). The separation of arsenic and antimony by precipitation of the former with sulphuretted hydrogen in strong hydrochloric acid (2 acid to 1 water) is to be recommended.

[1] *Cf.* Fresenius, *Quantitative Analysis*, 7th ed., vol. i., p. 490. On the precipitation of antimony by sulphuretted hydrogen in the presence of oxalic acid, see :—F. W. Clarke, *Chem. News*, 1870, **21**, 124; Lesser, *Z. anal. Chem.*, 1888, **27**, 218; Warren, *Chem. News*, 1890, **62**, 216; J. Clark, *J. Chem. Soc.*, 1892, **61**, 424; Henz, *Z. anorg. Chem.*, 1903, **37**, 1.

The small amount of copper sulphide remaining on the filter paper is dissolved in nitric acid, excess of ammonia added, and the copper determined by titration with potassium cyanide (*cf.* p. 181).

For the volumetric determination of the antimony in hard lead, the potassium bromate method (*cf.* Antimony, p. 286) is recommended and is carried out as follows:—About 1 g. of the metal, as finely subdivided as possible, is gently warmed in a flask with 20 c.c. of brom-hydrochloric acid (saturated solution of bromine in fuming hydrochloric acid), the contents being frequently shaken and warmed till completely decomposed or dissolved. When solution is completed, it is boiled until the vapours appear but slightly yellow in colour. After cooling somewhat, small pieces of sodium sulphite, about 3 or 4 g., are added in two to three portions with shaking, the solution boiled for about five minutes to drive off the sulphur dioxide, again boiled after the addition of 20 c.c. of strong hydrochloric acid and 40 c.c. of hot water, and the hot solution titrated with the potassium bromate solution. If much arsenic (4 to 5 per cent.) is present, it is necessary to boil down after the addition of the sulphite, take up with 20 c.c. of hydrochloric acid and a crystal of sodium sulphite, and then continue as above. A few drops of methyl orange are added as indicator, and when the red colour disappears, the titration is finished.

The results are very good and not influenced by the copper (0·5 per cent. at most) and small quantity of iron which are present in hard lead.

For the analysis of antimonial lead, sulphuric acid is frequently used as the solvent, and C. R. M'Cabe[1] considers the chief difficulty in this method is the absorption of antimonious sulphate by the precipitated lead sulphate. A suitable quantity of the sample (0·3 g. if the antimony content is over 12 per cent.) is dissolved in 10 c.c. concentrated sulphuric acid by heating carefully to boiling-point and, after cooling, the solution is diluted with about 50 c.c. water and boiled. The lead sulphate settles out, and the tin goes wholly into solution together with the greater part of the antimony. In a 10 to 12 per cent. antimony-lead alloy the revisers have found that 0·2 to 0·3 per cent. of the antimony remains insoluble.

The lead sulphate is filtered off, washed, dissolved in ammonium acetate and reprecipitated with sulphuric acid; the remaining antimony is now in solution. The lead sulphate is filtered off, washed, and may be weighed as sulphate if results of only moderate accuracy are required. Tin and antimony are determined in the combined filtrates, the former by reduction with iron and titration with standard iodine solution and the latter by titration with potassium permanganate solution.

Frequently the only determinations required are antimony and arsenic, but tin and copper are sometimes required in addition.

[1] *Ind. Eng. Chem.*, 1917, 9, 42.

These four elements are frequently determined on separate portions of the antimonial lead.

Silver in hard lead is always determined in the dry way (*cf.* Silver, p. 102) by scorification and cupellation.

Analysis of Hard Lead by the determination of the Specific Gravity.—The method recommended by G. Faunce,[1] which was not at first adopted on account of the inaccuracies in manipulation, has been investigated, and made practicable, by F. W. Küster, P. Siedler, and A. Thiel;[2] they obtained excellent results when the alloys under consideration solidified without formation of blow holes. On testing a hard lead, prepared by melting together 24 g. of pure lead and 6 g. of pure antimony in an atmosphere of hydrogen, the mean of sixteen determinations gave a specific gravity of 9·977, and the greatest difference from the actual antimony content worked out at 0·08 per cent. The calculation is based on the fact that hard lead containing 20 per cent. of antimony has a specific gravity of 9·977 (Faunce gives 9·974), and that in this alloy the specific gravity varies by 0·060 if the antimony content varies by 1 per cent. (according to Faunce).

In English works the following table is often used to give approximately the amount of antimony contained in antimonial lead:—

Spec. grav.	Per cent. Sb.	Spec. grav.	Per cent. Sb.
11·40	Nil	10·65	10·0
11·35	0·64	10·60	10·7
11·30	1·27	10·55	11·4
11·25	1·90	10·50	12·1
11·20	2·5	10·45	12·8
11·15	3·1	10·40	13·6
11·10	3·8	10·35	14·4
11·05	4·4	10·30	15·2
11·00	5·1	10·25	16·0
10·95	5·8	10·20	16·8
10·90	6·5	10·15	17·6
10·85	7·2	10·10	18·4
10·80	7·9	10·05	19·2
10·75	8·6	10·00	20·0
10·70	9·3		

V.—Analysis of Work Lead (*cf.* also p. 115).

The work lead as obtained directly from the ores contains 96 to 99 per cent. of lead, and is either refined, desilverised, and worked up into soft lead at the smelting works, or sent to special refining works. Since the content of impurities is much higher than in soft lead, a much smaller weight of sample suffices for the analysis, which may be carried out in exactly the same way as a soft lead analysis (*cf.* pp. 232 *et seq.*).

[1] *J. anal. Chem.*, 1887, 1, 123. [2] *Chem. Zeit.*, 1902, 26, 1107.

On account of the higher content of antimony, it is best dissolved in a mixture of nitric and tartaric acids.

H. Nissenson and B. Neumann[1] dissolve 10 to 50 g. according to the purity of the sample; for 10 g., 16 c.c. of nitric acid (sp. gr. 1·4), 60 c.c. of water, and 5 to 10 g. of tartaric acid is sufficient. The amount of tartaric acid given is sufficient to bring all the antimony in 50 g. into solution. The lead is precipitated out of this solution by the addition of sulphuric acid, 3 c.c. being added for every 10 g. of metal taken, and the solution filtered free from lead.

If the precipitation is done in a graduated flask, which is filled to the mark after cooling, and only a measured quantity of the solution as filtered through a dry paper taken for analysis, the volume of the lead sulphate (2·15 c.c. per 10 g. of lead) must be subtracted, in the manner given by Fresenius[2] for the analysis of soft lead.

The filtrate from the lead sulphate is evaporated and treated with sodium hydroxide and sodium sulphide as in the analysis of hard lead according to Nissenson and Neumann (p. 237). Arsenic, antimony, and tin are dissolved, separated, and determined as described. The residue contains copper, silver, bismuth, cadmium, zinc, iron, cobalt, and nickel, and is further treated as in the analysis of soft lead. Silver is determined in a separate weighing by cupellation (*cf.* pp. 110 *et seq.*).

The sulphur in work lead may be determined either by heating a fairly large quantity in a current of chlorine, collecting the sulphur chloride in a receiver and precipitating the sulphuric acid formed from the chloride by barium chloride, or by the sodium hydroxide method given on p. 236.

VI.—Lead Matte, Copper Lead Matte, Litharge and Red Lead

The silver in the smelting products which contain sulphur compounds of iron, lead, copper, etc., is always determined by dry methods or by a combined wet and dry method (*cf.* pp. 107 and 114). Lead and copper may be determined by the method given for copper ores containing lead (p. 190). The lead sulphate is then dissolved in ammonium acetate, the solution either precipitated with sulphuric acid or titrated with ammonium molybdate, or the sulphate converted into carbonate, which is dissolved in nitric acid and electrolysed, etc. (*cf.* Wet Methods of Assaying Lead Ores, p. 226). The copper may be determined either electrolytically or volumetrically (*cf.* Copper Assays for Ores, p. 190).

Litharge is analysed either by dry methods (*cf.* Lead Assays for Oxide Ores, etc. p. 225), or is fused with sodium carbonate and sulphur,

[1] *Chem. Zeit.*, 1895, 19, 1142. *J. Soc. Chem. Ind.*, 1895, 14, 1063.
[2] *Quantitative Analysis*, 7th ed., vol. ii., p. 373.

the melt lixiviated, arsenic and antimony determined in the solution, and lead, bismuth, copper, and iron determined in the residue by the methods given for the analysis of soft lead (pp. 232 *et seq.*). The amount of copper, which is generally small, may be determined colorimetrically (p. 189). The silver in the litharge is determined by the cupellation of the lead button obtained from the lead assay.

Red lead may be analysed by the methods given above for litharge, but sometimes it is necessary to determine in addition the percentage of Pb_3O_4 present. E. F. Figg[1] has described a modification of Liebig's[2] method which is carried out as follows:—One g. of the red lead is treated in a glass mortar with 40 c.c. of a saturated solution of sodium acetate in 5 per cent. acetic acid and a known excess (40 to 50 c.c. of $N/10$ solution) of sodium thiosulphate is added. The decomposition of the red lead proceeds slowly, and rubbing with a pestle is needed to complete it. The addition of a few c.c. of 5 per cent. potassium iodide solution facilitates the reduction of the more resistant particles of red lead and does not affect the titration. A few drops of starch solution are then added, and the excess of thiosulphate is titrated with $N/10$ iodine solution. The large excess of sodium acetate prevents the precipitation of lead iodide, and the end-point of the titration is sharp.

For the analysis of red lead for use as a pigment see p. 499.

VII.—Rich Lead Alloys

Tin-Lead Alloys rich in Lead.—One gram of the very finely divided alloy (rolled or scraped) is completely decomposed by warming in a covered porcelain or platinum dish with 20 c.c. of nitric acid of sp. gr. 1·2. One hundred c.c. of boiling water is then added, boiled for five minutes, and the tin oxide filtered off (*cf.* Bronze Analysis, p. 216). In the filtrate the lead is determined by evaporation with sulphuric acid, etc. Since the oxide of tin generally contains small quantities of lead, it is fused (after weighing) with sodium carbonate and sulphur, and any lead sulphide remaining after lixiviation with water converted into sulphate, which is weighed as such, and the corresponding amount of lead oxide deducted from the weight of impure stannic oxide.

Antimony is generally present in these alloys, and special precautions are then necessary, as the antimonious oxide will remain with the stannic oxide.

The tin and antimony are generally determined on separate portions of the sample, the former by solution of hydrochloric acid (assisted by a little chlorate if necessary), reduction by iron and

[1] *J. Soc. Chem. Ind.*, 1925, 44, 68T. [2] *Z. angew. Chem.*, 1901, 14, 828.

titration with iodine, and the latter, after solution in sulphuric acid, by titration with potassium permanganate solution. If desired, antimony may be determined by titration with potassium bromate after dissolving the alloy in hydrochloric acid to which bromine has been added.

Type metal, Bearing metal, etc. (Lead, Antimony, Tin).—Type metal, if it contains only a few per cent. of tin, is analysed like hard lead and dissolved in dilute nitric and tartaric acids (*cf.* p. 236). If it contains a higher content of tin, it is treated like anti-friction or white metal (*cf.* Tin, p. 265). Separate determinations of the metals are generally made as above.[1]

For determining the lead in alloys of lead, tin, and antimony, Parry[2] recommends the separation of the lead in alkaline solutions; the sulphide is then dissolved in hydrochloric acid with the addition of potassium chlorate, neutralised with ammonia, acidified with acetic acid, and titrated with potassium chromate.

Shot.—Shot contains from 0·2 to 0·8 per cent. of arsenic in addition to the lead. One gram of the shot, flattened by striking with a hammer, is dissolved in an Erlenmeyer flask by warming on the sand-bath with 20 c.c. of dilute nitric acid (sp. gr. 1·2). Ten c.c. of distilled sulphuric acid is added, and the solution boiled till sulphuric acid fumes are evolved. The cold residue is taken up with water, the lead sulphate filtered off, the filtrate boiled with 20 c.c. of sulphurous acid solution till no smell is recognisable, so as to reduce the arsenic, which is then precipitated by passing in sulphuretted hydrogen, and finally weighed as magnesium pyroarsenate.

Another method consists in dissolving 1 g. of the sample in 10 c.c. of concentrated sulphuric acid, cooling and diluting to 50 c.c., after which 100 c.c. of strong hydrochloric acid is added and the arsenic precipitated as sulphide by sulphuretted hydrogen.

The arsenic is often best determined by distillation at 120° with a solution containing 600 g. of calcium chloride, 300 g. of ferric chloride, and 600 c.c. of hydrochloric acid in 1 litre. The solution is boiled gently in the presence of antimony (*cf.* Estimation of Arsenic in Copper, p. 205) for twenty minutes, the distillate collected in a U-tube containing a little water, neutralised with ammonia, just acidified with hydrochloric acid, sodium bicarbonate added, and the solution then titrated with iodine. In the presence of a small quantity of sulphur a little solid mercuric chloride is put into the distillation flask to prevent sulphuretted hydrogen coming over and reprecipitating the arsenic in the U-tube.

[1] *Cf.* E. W. Hagmaier, *Chem. and Met. Eng.*, 1917, **16**, 84; *J. Inst. Metals*, 1917, **17**, 353.
[2] *Analysis of Ashes and Alloys*, 1908, p. 40.

VIII.—Waste Lead and Lead Ashes

Dry Method.—A large average sample of several kilograms weight is crushed and sieved, the proportion by weight of the flattened metal to the fines determined, each weighed out in this proportion so as to give a total assay sample of 50 g., and the metal in this reduced by fusion with sodium carbonate and charcoal, borax, and a covering of common salt in an iron or clay crucible (*cf.* p. 224). The impurities may be determined in the button of lead according to the methods given for the analysis of work lead and hard lead.

Many metallurgists prefer potassium ferrocyanide as a reducing agent, in which case 100 g. of metallics and fines are mixed thoroughly with 30 g. potassium ferrocyanide, 20 g. sodium carbonate and 10 g. of borax, and the mixture fused in a clay crucible. The metal and slag should always be allowed to solidify in the crucible, and this necessitates the breaking of the crucible to remove the metal button.

Wet Method.—Ten grams in all of a mixture of the metallic and the oxidised earthy portions is weighed, dissolved in 75 c.c. of nitric acid of sp. gr. 1·2 with the addition of a few grams of tartaric acid, the solution filtered after dilution with water, cooled, diluted to 500 c.c., 50 c.c. (corresponding to 1 g.) taken, the lead precipitated as sulphate by the addition of 5 c.c. of sulphuric acid, and weighed, as such. The impurities (antimony, copper, etc.) may be determined in the filtrate by the usual methods.

Lead ashes, which frequently contain lead sulphate, are treated with nitric acid, the residue washed, boiled with neutral ammonium acetate the filtrate diluted to 500 c.c., in 50 c.c. of which (corresponding to 1 g. of substance) the lead is precipitated with sulphuric acid.

IX.—Lead Slags

For the determination of lead in slags containing much lead, the dry assay gives sufficiently accurate results, but for slags containing little lead the volumetric method is necessary. From 2 to 5 g. of the finely powdered slag is dissolved in aqua regia, evaporated to dryness and baked to dehydrate the silica, taken up with dilute hydrochloric acid, diluted and filtered. The filtrate is nearly neutralised, and sulphuretted hydrogen passed in to precipitate the lead as sulphide. The precipitate is filtered off, washed, dissolved in nitric acid, and the solution evaporated with sulphuric acid to separate the lead as sulphate; this precipitate is then washed, dissolved in ammonium acetate, and titrated with ammonium molybdate (*cf.* p. 230).

F. S. Schimeska[1] has modified this method in order to adapt it to the rapid determination of lead in slags. Two g. of the slag is weighed into a 250 c.c. flask, 15 c.c. of water added, the whole boiled, and then 5 c.c. of concentrated hydrochloric acid added whilst agitating the flask. Immediately solution is complete, 140 c.c. of cold water is added, followed by 50 c.c. of saturated sulphuretted hydrogen water; the flask is then stoppered and vigorously shaken for fifteen seconds. The lead and copper present, which are precipitated in flakes of sulphide, are then filtered off. The occasional precipitation of zinc is of no consequence, and if small particles of slag remain undissolved, they will be attacked in the subsequent treatment. The addition of water to the hydrochloric acid solution of the slag is made quickly, so as to prevent the formation of gelatinous silica. The proportions of acid and water given above must be used, otherwise the lead will not be precipitated. The sulphide precipitate is filtered on to an asbestos filter attached to a pump, washed twice with water, transferred to a porcelain dish, 2 c.c. of concentrated nitric acid and 8 c.c. of concentrated sulphuric acid added, and the whole boiled until nitrous fumes cease to be evolved. After cooling, 40 c.c. of water is added, the liquid boiled and then filtered on paper or on an asbestos filter; any copper will be found in the filtrate. The filter and precipitate are boiled with ammonium acetate solution, and the solution which contains the lead titrated with ammonium molybdate solution.

X.—Lead Glazes

The Home Office gives the following method for the determination of the soluble lead in lead glazes:—A weighed quantity of the finely ground and dried material is shaken continuously for one hour with one thousand times its weight of 0·25 per cent. hydrochloric acid, and filtered after standing for one hour. The lead is precipitated as sulphide in an aliquot part of the filtrate, and then weighed as sulphate. A suitable quantity for the test is 0·5 g. of the dried glaze.

[1] *Eng. and Min. J.*, 1910, **89**, 467.

BISMUTH.

Bismuth is produced in part directly from ores and partly from intermediate products arising in the working up of work lead containing bismuth (litharge, furnace bottoms, and cupels containing bismuth).

Of the numerous minerals containing bismuth, the following ores are of practical importance:—

Native Bismuth, often containing some arsenic.

Bismuthite, Bi_2S_3, with 81·2 per cent. Bi.

Emplecite, $CuBiS_2$, containing 62·0 per cent. Bi and 18·9 per cent. Cu.

Bismuth Ochre, Bi_2O_3, with 89·6 per cent. Bi, containing always some H_2O, CO_2, and Fe_2O_3, and, less frequently, As_2O_5 also.

The ores, metallurgical products containing bismuth, and the bismuth alloys are always analysed by wet methods; the dry assays[1] for ores, etc., are, on account of the greater volatility of bismuth, less accurate than the corresponding lead assays, and an impure metal always results, since lead, copper, antimony, arsenic, iron, etc., are easily retained by the bismuth. Only the noble metals in the ores, etc., are determined by dry assays (*cf.* Silver).

I.—Analytical Methods for Ores and Metallurgical Products

Fresenius' Method.[2]

This method is suited to all ores, and takes into consideration the presence of bismuth, lead, copper, silver, gold, antimony, arsenic, tin, iron, cobalt, nickel, zinc, sulphur, and tellurium.

For the determination of the bismuth, 2 to 5 g. of the very finely ground ore, dried at 100°, is dissolved in nitric acid of sp. gr. 1·3 (30 to 75 c.c.) with the addition of 2 to 5 g. of tartaric acid, in a flask placed in a slanting position on a sand-bath. The solution, somewhat diluted, is filtered, the filtrate diluted to 100 or 250 c.c., and sulphuretted hydrogen passed in to saturation in the cold. The precipitate is filtered off, washed with sulphuretted hydrogen water, and boiled with sodium sulphide solution. The insoluble sulphides are collected on a filter paper, washed, dissolved by warming with dilute nitric acid, and the solution filtered (from sulphur and any lead sulphate). Sodium carbonate is added to the nitric acid solution (of bismuth, lead,

[1] *Cf.* Beringer, *Text-book of Assaying*, 1921, 15th ed., p. 221.

[2] Fresenius, *Quantitative Analysis*, 7th ed., vol. ii., p. 418.

copper, silver) until a permanent precipitate is formed, and then a few grams of pure potassium cyanide. After digesting at a gentle heat for some time (about one hour), the bismuth and lead carbonate precipitate, which retains alkali, is filtered off.

For the separation of the bismuth from the lead, the carbonates are dissolved in hot, dilute nitric acid, the solution evaporated with a good excess of sulphuric acid (about 4 c.c. for a 1 g. sample), the residue taken up with a liberal supply of dilute sulphuric acid and well boiled, the lead sulphate, free from bismuth, filtered off and washed with 10 per cent. sulphuric acid. The acid bismuth sulphate solution is diluted, a slight excess of ammonia added, and after gentle warming, the bismuth hydroxide filtered off and washed for a short time. The impure hydroxide, contaminated with some basic sulphate, is dissolved in a little nitric acid, the pure hydroxide precipitated as above with a slight excess of ammonia, and, after drying, converted into oxide by ignition. $Bi_2O_3 \times 0{\cdot}8969 = Bi$.

If the amount of bismuth is small (up to 0·1 g.), the washed hydroxide is dissolved off the filter paper by dropping hot, dilute nitric acid on to it from a pipette. The solution is evaporated on the water-bath in a weighed porcelain crucible, the crucible then heated on a sand-bath, and the nitrate finally completely decomposed by ignition over a free flame.

Larger quantities of the hydroxide are dried, separated as completely as possible from the filter paper, the portion that remains attached dissolved off as above, the solution evaporated, and then the dried and ignited bismuth hydroxide added.

The separation by means of sulphuric acid is satisfactory, provided plenty of acid is used, and the residue is not treated with too much water. Fernandez-Krug and Hampe give the following method for the detection of any retained basic bismuth sulphate:—The washed lead sulphate is washed off the filter paper, the water removed by evaporation, and the sulphate converted into chloride by warming with concentrated hydrochloric acid. After cooling, about 50 c.c. of absolute alcohol is added to the small volume (about 5 c.c.) of hydrochloric acid solution (H. Rose's method), the solution stirred, and after standing for a short time, the alcoholic solution containing all the bismuth (present in the lead sulphate) as chloride is filtered. On diluting with a large volume of water, the bismuth is precipitated as oxychloride, and thus separated from any trace of lead chloride which may have gone into solution.

H. Rose's[1] method of separation, depending on the insolubility of lead chloride in strong alcohol, is less convenient to carry out than the foregoing separation by means of sulphuric acid. The dilute bismuth

[1] Rose-Finkener, *Quantitative Analyse*, p. 165.

and lead nitrate solution, corresponding to a sample of about 1 g., is evaporated to quite a small volume (3 c.c.), rather more strong hydrochloric acid than is necessary for the formation of the chlorides (5 c.c.) added, and stirred for a few minutes at a very gentle heat. After cooling, 25 c.c. of absolute alcohol is added, the solution stirred, the lead chloride filtered off after some time and washed, first with absolute alcohol and a few drops of hydrochloric acid, and finally with absolute alcohol. By diluting the filtrate from the lead chloride with a quantity of water (500 c.c.), all the bismuth is precipitated as oxychloride, which, after standing for twenty-four hours, is filtered on to a tared, dried filter paper, dried at 110°, and weighed as bismuth oxychloride. $BiOCl \times 0{\cdot}8024 = Bi$.

It is quicker to drive off the greater part of the alcohol in the bismuth solution by gently warming, and then precipitate the bismuth hydroxide by a slight excess of ammonia, and weigh as oxide as above.

The determination of the remaining constituents in bismuth ores is fully described by Fresenius (*loc. cit.*). The noble metals are always determined by dry assays (*cf.* Silver and Gold).

The analytical methods, which appear somewhat complicated, may often be much simplified, according to the composition of the ores. In, for instance, bismuthite, containing only copper pyrites ($CuFeS_2$) as impurity, the first precipitate, with sulphuretted hydrogen ($Bi_2S_3 + xCuS$), naturally need not be extracted with sodium sulphide solution; the copper sulphide is preferably removed by potassium cyanide solution, the residue of bismuth sulphide dissolved in hot, dilute nitric acid, a slight excess of ammonia added, and the precipitated hydroxide converted into bismuth oxide and weighed as such.

Bismuth ochre, if it contains only iron and gangue as impurities. is still simpler to analyse. The filtered diluted nitrate solution is saturated with sulphuretted hydrogen and the bismuth sulphide treated as given for bismuthite. Bismuth ochre containing arsenic is best dissolved in hydrochloric acid, the gangue filtered off, and the bismuth and arsenic precipitated in the somewhat diluted solution by sulphuretted hydrogen, etc. (Bismuth arsenate dissolves readily in hydrochloric acid and in hot, strong nitric acid; it is insoluble in cold, dilute nitric acid.) The precipitation of the bismuth as oxychloride by dilution of the hydrochloric acid solution is less reliable.

Hampe's Methods.[1]

One gram of the finely ground and dried slag is digested in a platinum dish with about 15 c.c. of nitric acid for a long time, and then 10 c.c. of concentrated hydrofluoric acid is added. If the slag is dissolved, a few drops of concentrated sulphuric acid are added, and the

[1] *Chem. Zeit.*, 1891, 15, 410; *J. Chem. Soc. Abstr.*, 1892, 62, 919.

contents of the dish are evaporated to dryness. The residue is again dissolved in nitric acid and any graphite (from the crucibles) filtered off. After neutralising the filtrate with ammonia, bismuth, lead, and iron, as well as the small quantities of alumina and calcium, are precipitated with ammonium carbonate, the solution boiled, and the precipitate filtered off. The precipitate is dissolved in nitric acid and sulphuretted hydrogen passed into the solution. The precipitated lead and bismuth sulphides need not be treated with sodium sulphide, since antimony is present only in traces, but are at once dissolved in nitric acid. The solution, filtered free from sulphur, is precipitated with ammonium carbonate, taking the usual precautions, the precipitate containing all the lead and bismuth filtered off, dissolved in hydrochloric acid, and the solution of lead and bismuth chlorides evaporated to complete dryness. The lead chloride is then dissolved by much hot water, whilst the bismuth is precipitated as oxychloride and filtered off. The bismuth oxychloride is dissolved in nitric acid, precipitated with ammonium carbonate, filtered, and the filter paper with the precipitate dried. When dry, as much of the bismuth carbonate as possible is removed from the paper and set on one side. Any carbonate remaining attached to the filter paper is dissolved off in nitric acid, the solution evaporated to dryness in a weighed porcelain crucible, the remainder of the precipitate then added and carefully ignited, after which the bismuth oxide is weighed.

The Electrolytic Determination of Bismuth.

According to O. Brunck's[1] modification of K. Wimmenauer's method the electrolytic determination of bismuth is carried out as follows:— A nitrate solution, free from chloride, is prepared containing not more than 2 per cent. of acid. A maximum E.M.F. of 2 volts is used. With solutions containing more than 1 per cent. of metal, a current density of 0·5 ampère per 100 sq. cm. and over may be employed; with weaker solutions it is well not to use more than 0·1 ampère. At the commencement of the electrolysis the solution is heated to 70° or 80°, and allowed to cool down of itself whilst the electrolysis proceeds. The deposition on a Winkler gauze cathode is complete in from two to three hours. The deposited metal is of a light reddish grey colour, dense and adhesive. The washing must be done without breaking the circuit, otherwise appreciable quantities of bismuth are redissolved.

The rapid precipitation of bismuth with the use of a rotating anode and mercury cathode is described by E. F. Smith[2] (*cf.* Vol. I., p. 108).

[1] *Ber.*, 1902, **35**, 1871; *Z. angew. Chem.*, 1902, **15**, 735; *J. Chem. Soc. Abstr.*, 1902, **82**, 478.
[2] *Electro-Analysis*, p. 99.

The Colorimetric Determination of Small Quantities of Bismuth.[1]

Stone[2] found that an excess of potassium iodide, added to a dilute sulphuric acid solution of bismuth, produces a yellow colour the intensity of which is directly proportional to the amount of bismuth present. As it is not necessary to obtain the bismuth as a pure salt, practically all the sources of trouble in separation are absent. The object is to first obtain a solution free from large quantities of lead, copper, tin, antimony, gold, and silver, then to precipitate the bismuth as oxychloride, together with possible traces of these metals, arsenic, or tellurium, and to apply the colorimetric method to the solution of this precipitate in sulphuric acid. *Ores, mattes*, etc., are dissolved in hydrochloric and nitric acids, the silica removed as usual, and the filtrates treated as described under copper or lead, with the exception that hydrochloric acid must be removed by evaporating with sulphuric acid to precipitate any lead. Samples containing large amounts of tin, antimony, or arsenic may be fused with a mixture of equal parts of sodium carbonate and sulphur, and the melt dissolved in water and boiled, when all the bismuth is found in the black residue on filtering, and may be dissolved in nitric acid. Ten grams of *copper* is dissolved in 60 c.c. of nitric acid (1 : 1), the solution diluted with 150 c.c. of water, and a saturated solution of sodium carbonate added till a slight permanent precipitate forms; 1 c.c. is added in excess, which brings down all the bismuth and some copper, and the whole is boiled for five minutes and allowed to settle. The precipitate is filtered off, washed once, and dissolved through the paper back into the original beaker with hydrochloric acid, the bismuth precipitated as basic chloride and, if necessary, reprecipitated to separate the remaining copper as directed below. Ten grams of *refined lead, base bullion*, etc., are dissolved in 80 c.c. of water and 20 c.c. of nitric acid (sp. gr. 1·42), boiled to precipitate most of the tin and antimony, and a small excess of sodium chloride solution (1 : 200) added to precipitate the silver. The lead is precipitated by adding 60 c.c. of boiling sulphuric acid (1 : 20), drop by drop, to the boiling solution, with constant stirring, and then 30 c.c. of sulphuric acid (1 : 3) in excess. The liquid is cooled and allowed to stand an hour, filtered, and the precipitate washed several times by decantation with sulphuric acid (1 : 20). Five c.c. of strong hydrochloric acid is added to the filtrate, and a slight excess of ammonia, then a few drops of hydrochloric acid (1 : 5), till a drop of methyl orange in the solution indicates that it is just acid, when it is boiled for a minute and allowed to stand in a warm place for an hour. The precipitate is collected on a filter and washed twice, and the acidity of the filtrate readjusted to see if it is free from bismuth, or

[1] Rowell, *J. Soc. Chem. Ind.*, 1908, **27**, 102. [2] *Ibid.*, 1887, **6**, 416.

it is tested with potassium iodide. The filter and precipitate are now pulped with 10 c.c. of sulphuric acid (1 : 3), 30 c.c. of water added, and the solution boiled, cooled thoroughly to separate any lead sulphate, and filtered through a Hirsch's or similar funnel on the filter pump, and the paper pulp carefully washed with sulphuric acid (1 : 20). All, or a suitable fraction of the filtrate, containing possibly antimony, arsenic, tellurium, iron, and traces of lead, copper, or silver, and not more than 2 or 3 mg. of bismuth, is placed in one of a pair of 10-inch Nessler tubes, and 5 c.c. of sulphuric acid (1 : 3) with some water in the other, and both are shaken up after the addition of 5 c.c. of potassium iodide (20 per cent.) and ten drops of sulphurous acid (one part saturated solution to two parts water). The blank tube is titrated with a standard solution of bismuth (made by dissolving 0·1 g. of pure metal in 10 c.c. of strong nitric acid and making up to 1000 c.c. with water), till the colour of about 120 c.c. matches that of an equal volume of the test solution.

Arsenic, antimonic, and nitrous acids and ferric salts, or excessive quantities of sulphuric or nitric acids, sulphates, or nitrates throw out iodine, which is removed by prolonged boiling, or more easily by sulphurous acid. A hot solution of bismuth iodide is a little darker than when cold, and in the presence of tellurium, boiling permanently but only slightly darkens the colour. A large excess of sulphurous acid produces an iodine colour, which is removed by the addition of more potassium iodide. Alkalis in excess, ammonium acetate, hydrochloric acid, and chlorides bleach the colour, but the addition of more sulphuric acid or potassium iodide restores it. Experiments show that any precipitates of copper or silver iodides or metallic tellurium may be filtered off without losing any bismuth, but that lead iodide carries a large proportion of the bismuth with it. Two milligrams of lead, copper, or silver may be present in the Nessler tube without giving a precipitate or darkening the colour, but a careful watch must be kept on this, as a very slight precipitate considerably darkens the tint.

Two operators using a simple form of colorimeter clearly and correctly distinguished between the following quantities of bismuth, which were unknown to them, and also between various other intermediate quantities in 125 c.c. of solution:—None and 0·00001 g., 0·00020 g. and 0·000225 g., 0·0010 g. and 0·00105 g., 0·0020 g. and 0·0021 g., 0·0030 g. and 0·0031 g.; 0·00001 g. represents one part in twelve and a half millions, and these figures show that this colour test is at least twice as delicate as Nessler's test for ammonia, and that the limit of error is within 5 per cent. of the bismuth present, which means that a result of 0·001 per cent. is correct to within 0·00005 per cent., or a result of 0·10 per cent. is within 0·005 per cent. of the truth.

The apparatus is described and figured in Vol. I., p. 181.

II.—Analysis of Commercial Bismuth

For many years bismuth has been put on the market in a very pure condition, since it is chiefly manufactured for pharmaceutical preparations and must comply with the requirements of the Pharmacopœia (as regards its freedom from arsenic, etc.). Smaller quantities of bismuth are used for the preparation of fusible alloys (bismuth with tin, lead, and also cadmium), which are used in safety appliances for steam boilers and for other purposes.

Crude bismuth is frequently largely contaminated by antimony, arsenic, copper, lead, and sulphur.

Qualitative Detection of the Impurities.—Two grams of the metal is dissolved by warming in 30 c.c. of nitric acid (sp. gr. 1·2); if a permanent milkiness of antimony or tin is produced (bismuth arsenate dissolves), 30 c.c. of water is added, the solution boiled for a few minutes, and the precipitate, to be investigated later, filtered off. Any silver in the filtrate is precipitated as chloride by a few drops of hydrochloric acid, and the filtrate from the silver chloride evaporated to quite a small volume (3 to 5 c.c.). Ten cubic centimetres of fuming hydrochloric acid is then added, well stirred, 30 c.c. of absolute alcohol added, again well stirred, allowed to stand a quarter of an hour, and the separated lead chloride filtered off. The filtrate is evaporated on the water-bath to 10 c.c., 150 c.c. of boiling water added, the bismuth oxychloride filtered off, the filtrate from which is concentrated by evaporation to about 20 c.c., and one-half of the solution saturated with ammonia: iron is precipitated as brown flocculent hydroxide; copper gives a blue solution. A fair quantity of the oxychloride precipitate is dissolved in the other half of the filtrate from the bismuth oxychloride by addition of hydrochloric acid, and the solution tested for arsenic in a simple Marsh apparatus. Arsenic may also be recognised by the blowpipe; alloyed with an equal weight of zinc, bismuth containing arsenic evolves hydrogen containing arseniuretted hydrogen in a Marsh apparatus.

Quantitative Analysis.—On solidifying, that part of the metal which solidifies last is very rich in impurities, and is squeezed out of the bar or cake and solidifies on the surface in the form of a protuberance. In sampling, this protuberance is removed by a chisel, its weight and the ratio of its weight to that of the total weight of the ingot determined, and then (after pulverising the protuberance) proportional quantities of the impure protuberance and of the purer remaining part of the ingot mixed for the sample.

Three grams of the sample is dissolved in 50 c.c. of nitric acid (sp. gr. 1·2) and 3 g. of tartaric acid in a flask over a free flame, the nitrous fumes boiled off, the solution cooled, transferred to a beaker, diluted to 200 to 300 c.c., and sulphuretted hydrogen passed in for a

long time without warming. After several hours the sulphides are filtered off, washed with sulphuretted hydrogen water, and the filtrate again saturated with sulphuretted hydrogen, and gently warmed for twenty-four hours. By this treatment a further small quantity of arsenic sulphide may separate, which is filtered off, dissolved off the filter paper by a saturated solution of ammonium carbonate and again reprecipitated by adding excess of hydrochloric acid, and warming. In the filtrate from the sulphuretted hydrogen precipitates, the iron is precipitated by saturating with ammonia, adding ammonium sulphide, and warming. The iron sulphide is filtered off, dissolved in hydrochloric acid, the solution evaporated, the iron oxidised with bromine water, and then precipitated as hydroxide by ammonia, and either weighed as ferric oxide or titrated.

The sulphides are digested for several hours with yellow sodium sulphide solution. A trace of bismuth may be dissolved. It will be found with the arsenic and other sulphides, and is removed together with traces of copper, by carefully treating the ammoniacal solution (to which some tartaric acid is added) with sulphuretted hydrogen water according to Finkener's method. The solution containing the antimony, arsenic, and possibly tin, is filtered, the sulphides reprecipitated in the filtrate by acidifying with dilute sulphuric acid, and warming for a good time on a boiling water-bath. They are then filtered off, washed with hot water to which some ammonium acetate and acetic acid is added, finally once with pure water, then with absolute alcohol. In order to remove as much as possible of the sulphur from the precipitate, the filter tube is corked up, carbon bisulphide poured on to the paper, and allowed to stand for several hours. After running off the carbon bisulphide, and after the residue left on the paper has evaporated, the sulphides are dissolved off the filter paper in warm dilute hydrochloric acid to which some potassium chlorate is added. To the solution strong hydrochloric acid is added, and the arsenic precipitated as sulphide by saturating with sulphuretted hydrogen for a long time. The sulphide is filtered off on to an asbestos filter, and dissolved in hydrochloric acid and potassium chlorate; to this solution the solution of the small amount of arsenic previously precipitated (see above) is added, and then concentrated by evaporation. The concentrated solution thus obtained is saturated with ammonia, magnesia mixture and alcohol added, and the ammonium magnesium arsenate so obtained ignited, and finally weighed as magnesium pyroarsenate (*cf.* Arsenic, p. 274).

To the strongly acid filtrate from the arsenic sulphide some tartaric acid is added, the solution much diluted, antimony and tin precipitated as sulphides by passing in sulphuretted hydrogen, and separated and determined as described on p. 267. Tin is only very seldom found in commercial bismuth.

The sulphides insoluble in sodium sulphide solution are first washed with dilute sulphuretted hydrogen water, then washed into a dish with a very little water, a few grams of solid potassium cyanide added, gently warmed for half an hour, the solution containing all the copper and silver filtered, and the residue washed first with potassium cyanide solution and then with dilute sulphuretted hydrogen water. The solution containing the copper and silver is acidified with nitric acid, warmed until all the separated cuprous cyanide is redissolved, and the silver cyanide filtered off. The filtrate is evaporated with sulphuric acid until the hydrocyanic acid is completely driven off, the residue dissolved in a little water, and the small amount of copper precipitated by sulphuretted hydrogen water. The copper sulphide is filtered off and determined as cupric oxide. After drying, the silver cyanide is placed together with the filter paper in a weighed porcelain crucible, strongly ignited with good access of air, and the metallic silver weighed.

The bismuth sulphide, still mixed with some lead sulphide, is dissolved in dilute nitric acid, the somewhat diluted filtrate filtered free from sulphur, and evaporated first in a porcelain dish, and finally in a beaker to a very small volume (about 5 c.c.). To the cold, syrupy liquid, fuming hydrochloric acid is added (according to H. Rose's method[1]) in such quantity that a portion of the clear solution does not become immediately turbid on the addition of a few drops of water; for 2 g. of bismuth 7 c.c. of pure fuming hydrochloric acid suffice. A few drops of dilute sulphuric acid are then added, and the solution allowed to stand for some time, with frequent stirring, so as to convert the lead chloride, which separates at first, into sulphate. Thirty c.c. of alcohol (sp. gr. 0·8) is then added to the contents of the beaker, which are well stirred, and the settled lead sulphate filtered off after a few hours. It is washed first with alcohol to which a few drops of hydrochloric acid are added, then with water, dried, etc. (*cf.* Lead, p. 226), and finally weighed as lead sulphate. The alcoholic bismuth chloride solution is diluted with 500 c.c. of water and the bismuth precipitated as oxychloride, which is contaminated with some basic sulphate. It is filtered off, dissolved in dilute nitric acid, the solution neutralised with ammonia, ammonium carbonate added, boiled, the bismuth carbonate filtered off, washed with hot water, and finally weighed as oxide (*cf.* Hampe's method of determining bismuth, etc., p. 247).

If it is desired to separate the lead, which is generally present in very small quantity, from the bismuth by means of sulphuric acid, a large quantity of the latter must be added to the nitrate solution of the two sulphides, and the solution evaporated, etc., otherwise insoluble basic bismuth sulphate is readily formed.

[1] Rose-Finkener, *Quantitative Analyse*, vol. ii., p. 164.

Selenium and *Tellurium* are found in Bolivian and certain other kinds of bismuth. For their determination, 10 to 20 g. of the metal is dissolved in a slight excess of nitric acid, the cold solution diluted with double the volume of water (no basic nitrate should separate), sulphur dioxide passed in for several hours, and after standing for two and a half hours, the precipitate containing silver, selenium, and tellurium filtered off, and treated further as described for the determination of selenium and tellurium in commercial copper, p. 211.

Sulphur is determined (in crude bismuth) by dissolving 10 g. in aqua regia, diluting, warming, and adding hot, dilute barium chloride solution. After standing for twenty-four hours the cleared solution is poured off, the precipitate of barium sulphate and silver chloride brought on to a double filter paper, washed with dilute hydrochloric acid, then with water, finally with ammonia, and the barium sulphate weighed.

The Noble Metals (silver and sometimes a trace of gold) are best determined by the cupellation of 50 g. of metal in a correspondingly large cupel (*cf.* Silver). E. A. Smith[1] has determined the noble metals in different kinds of bismuth, and found, *e.g.*, in an assay of Australian bismuth, 0·011 per cent. of gold and 0·3319 per cent. of silver.

III.—Analysis of Bismuth Alloys[2]

As only the fusible alloys need be considered, the analysis of Wood's metal (bismuth, lead, tin, and cadmium) will serve as an example.

One gram of the metal, as finely divided as possible, is completely decomposed by warming on the water-bath in a covered porcelain dish with 15 c.c. of nitric acid, the solution evaporated to dryness, the residue taken up by warming with very dilute nitric acid, the tin oxide (contaminated with lead oxide and bismuth oxide) filtered off, washed with boiling water, ignited, and weighed. In order to determine the impurities, the weighed, impure tin oxide is fused with six times its weight of sodium carbonate and sulphur (or dehydrated sodium thiosulphate), the melt lixiviated with hot water, and the sulphides of lead and bismuth determined in the residue by H. Rose's method, as described on p. 253. The lead is determined as sulphate and the bismuth as oxide, and the weight of the two oxides subtracted from the weight of the impure tin oxide.

The filtrate from the stannic oxide is evaporated to dryness, and the nitrates of bismuth, lead, and cadmium converted into the chlorides by twice evaporating on the water bath with about 20 c.c. of hydrochloric acid. The lead is separated as chloride by H. Rose's method (p. 246), and collected on a weighed filter paper. The alcoholic solution of

[1] *J. Soc. Chem. Ind.*, 1893, **12**, 316.

[2] *Cf.* Fresenius, *Quantitative Analysis*, 7th edition, vol. ii., p. 420; also, Jannasch and Etz, *Ber.*, **25**, 736 (Bromine Method); *J. Chem. Soc. Abstr.*, 1892, **62**, 385, 540, 754.

bismuth and cadmium chlorides is very largely diluted and the precipitate of pure bismuth oxychloride filtered off on to a weighed paper, and weighed after drying for several hours at 100°. The cadmium chloride solution (filtrate from bismuth oxychloride) is evaporated in a dish with a slight excess of sulphuric acid to quite a small volume, the solution removed to a weighed porcelain or platinum crucible, again evaporated, the slight excess of sulphuric acid driven off, the residue ignited moderately strongly, and finally weighed as cadmium sulphate. The cadmium may also be precipitated in the filtrate from the bismuth oxychloride by sulphuretted hydrogen, the cadmium sulphide dissolved in hot dilute nitric acid, and the solution evaporated with a slight excess of sulphuric acid, etc., as above. $PbCl_2 \times 0.74 = Pb$; $CdSO_4 \times 0.5392 = Cd$.

TIN.

Analyses of the following ores and products are frequently required: —Cassiterite (tin-stone), tin pyrites, the commercial metal, tin alloys, tinplate waste, tin ashes and residues, and tin slags.

The tin content in pure ores is sometimes determined by the dry methods; all other materials are submitted to wet analysis. The noble metals in tin-stone are determined by scorifying with a large quantity of assay lead (thirty times the weight), and cupelling, or the pot assay method may be used (*cf.* pp. 102 and 134).

Tin Ore.—Tin-stone, SnO_2, which contains 78·7 per cent. of tin, is the only ore of importance; it is contaminated by gangue, by wolframite, arsenical pyrites, molybdenite and pyrites, and less frequently by galena and zinc blende. In the secondary formation, as stream-tin, it frequently occurs along with other specifically heavy minerals, such as wolframite, titaniferous iron ore, columbite, spinelle, granite, etc. and also frequently contains some gold.

Tin Pyrites, Cu_2FeSnS_4, which contains 24 to 31 per cent. of tin and 24 to 30 per cent. of copper, is only seldom found (Cornwall, Tasmania), and then not in large quantities.

I.—Dry Assay of Tin-Stone[1]

Well-dressed, rich ores may be reduced to metal with good results; poor ores are first freed from the greater part of the gangue by washing, which is easily carried out owing to the high specific

[1] For the standard methods of Tin Assaying as used in the laboratory of the Eastern Smelting Co., Penang, see *A Text-book of Assaying*, C. and J. J. Beringer, 15th edition, 1921, p. 453.

gravity of cassiterite (6·8). To obtain as pure a metal as possible from the assay, the metallic impurities (iron, tungsten, etc.) are separated beforehand as far as possible. In many cases this "washing" assay is the only one required, the result being returned as "black-tin."

The fusion of the ore with reducing and fluxing agents is carried out in fire-clay crucibles in a wind furnace. Mitchell's potassium cyanide assay gives the best results, although a carbon reduction method is largely used in Cornwall.

Purification of the Sample of Ore.—For the purpose of cleaning, the ore may be treated with aqua regia alone, or with sulphuric acid, followed by aqua regia. The former is always used when lead or wolfram are present, but a preliminary treatment with sulphuric acid is necessary with ores containing titanium minerals.

In using the aqua regia method 10 g. of the finely divided ore is placed in a beaker, 60 c.c. hydrochloric acid added and the contents well shaken, after which 20 c.c. nitric acid is added and the beaker placed on a hot plate to allow the contents to digest for about one hour.

After cooling, about 100 c.c. water is added, the residue allowed to settle and then filtered on to double papers. If wolfram is present, it is removed from the residue by washing with ammonia (1 to 1) or with 10 per cent. solution of sodium hydroxide, after which the washing is continued with water, dilute hydrochloric acid, and finally with water.

In the presence of titanium minerals and when the concentrate is somewhat low grade, 10 g. is treated with 7 c.c. of water in order to moisten the material, then 15 c.c. of sulphuric acid added, the whole well shaken and allowed to digest on a hot plate. On the evolution of sulphuric acid fumes the beaker is removed from the plate and allowed to cool. When cold, 30 c.c. hydrochloric acid and 10 c.c. nitric acid are added, the contents well shaken, the beaker returned to the hot plate and its contents allowed to digest until impurities are in solution. The beaker is then removed, allowed to cool, 50 c.c. water added, the residue allowed to settle, the solution filtered through double papers and the residue washed and dried.

1. *The Assay by Fusion with Potassium Cyanide.*—About 5 g. of potassium cyanide (98 per cent.) broken up into coarse lumps is placed in the bottom of a clay crucible 12 to 15 cm. high, 10 g. of the ore, or the total residue from the preliminary cleaning, intimately mixed with 30 g. of potassium cyanide, then introduced, a covering of 5 g. of potassium cyanide added on the top, and the crucible placed in a moderately hot fire. The fire is kept as hot as possible during the short duration of the assay (fifteen to twenty-five minutes) without

allowing the potassium cyanide to boil. The crucible is then removed from the fire, its contents poured into a warmed mould, the slag washed away by water, and the button of metal weighed.

In place of the above charge the following is sometimes employed:—10 g. of ore, 20 g. potassium cyanide, and 3 g. of charcoal.

The button obtained is naturally not absolutely pure; it always contains small quantities of iron, etc. Any gold in the ore goes completely into the button of tin, as was shown by Pufahl;[1] by dissolving the flattened or rolled tin in hydrochloric acid the gold remains as a brown powder.

2. *The Cornish Assay.*—As this method is only suitable for concentrates it is necessary to carry out a preliminary concentration of ores followed by acid cleaning.

For the assay 100 g. of concentrate in a fine state of division is mixed with 15 to 20 g. powdered anthracite and charged into a previously annealed plumbago crucible of suitable size. The charged crucible is placed in a moderately hot wind furnace and heated to bright redness (1000°) for about thirty minutes. When the charge has settled down the crucible is gently shaken, removed from the fire, and the charge is poured into a mould. The lump of tin is removed and the remainder is pounded in an iron mortar, the larger tin-prills which have been flattened removed by the aid of a 30-mesh sieve, the fines re-ground and a further quantity of tin recovered by the use of a 60-mesh sieve. The very fine metallic tin left in the material passing the latter sieve is recovered by washing in a large porcelain dish, dried, added to the prills and the main button and weighed.

II.—Wet Assay of Ores, etc.

Owing to the refractory nature of tin-stone, the first step in the wet assay of ores, etc., consists of an operation by which the tin is rendered soluble in acids.

A method suitable for practically all ores consists in cleaning the material and then reducing the tin to the metallic state by strong ignition in a porcelain or silica tube in a current of hydrogen or coal gas,[2] dissolving the reduced metal in hydrochloric acid and determining the tin gravimetrically or volumetrically.

A method specially suitable for ores containing tungsten and recommended by Donath and Müllner[3] for the separation of tin oxide from

[1] *Berg u. Hütten. Zeit.*, 1886, 45, 174. *Cf.* Bannister, *Trans. Inst. Min. and Met.*, 1905-6, 15, 513.
[2] *Cf. Text-book of Assaying*, C. and J. J. Beringer, 15th edition, 1921, p. 283.
[3] *Monatsh.*, 1888, 8, 647. *J. Chem. Soc. Abstr.*, 1888, 54, 531. *Cf.* also T. Moore, *Chem. News*, 1893, 67, 267.

tungstic acid, consists in mixing the material with zinc dust or zinc filings and strongly igniting in a covered porcelain crucible for fifteen minutes. The product is treated with dilute hydrochloric acid and boiled until evolution of hydrogen ceases, and then treated with potassium chlorate until the blue tungstic oxide is oxidised to tungstic acid. Water is added to the solution, which is filtered after twenty-four hours; the filtrate contains the tin.

Beringer[1] has modified the method of Donath and Müllner by using a mixture of zinc oxide and metallic zinc for the reduction of the tin. The quantity of material taken for the assay varies with its nature, 0·25 or 0·5 g. being sufficient in the case of concentrates, whereas 2·5 to 5 g. is necessary for ores and 5 to 10 g. for tailings. A little zinc oxide is placed in the bottom of a porcelain crucible and about 4 g. of sheet zinc cut into small pieces is placed on this; the weighed charge of ore is mixed with a little zinc oxide and placed in the crucible. The total amount of zinc oxide should be about 2 g. The crucible is covered with a lid and heated to about 900° in a Bunsen furnace or muffle. After allowing to cool, the contents of the crucible are dissolved in hydrochloric acid and the solution used for the determination of tin.

Hutchin[2] has modified Beringer's method by substituting lime or calcium carbonate for the mixture of zinc oxide and zinc. The proportion of lime suggested is 1·5 g. for 1 g. of concentrate and 2 g. for 2·25 g. of somewhat low grade ore; more may be used if it is necessary. In carrying out this method too high a temperature must be avoided, and as the products of combustion of a gas flame are necessary for the reactions by which calcium stannate is formed, an alundum crucible, heated over a Teclu burner, is recommended. The reactions are complete in about fifteen to twenty minutes and, after cooling, the charge is removed from the crucible, dissolved in hydrochloric acid, and the solution further treated for the determination of the tin.

The Pearce-Low[3] method, which is largely used for tin ores and slags, consists in fusing the finely ground material with about ten times its weight of sodium hydroxide[4] in an iron crucible, pouring the molten mass into a clean nickel crucible, from which it is easily detached, taking up with water, acidifying with hydrochloric acid and determining the tin in the solution.

J. Darroch and C. Meiklejohn[5] use the following method for all tin ores, slags, etc.:—Half a gram of the material is fused in a nickel

[1] *Text-book of Assaying*, 15th edition, 1921, p. 285.

[2] *Trans. Inst. Min. and Met.*, 1914, 23, 269.

[3] A. H. Low, *Technical Methods of Ore Analysis*, 5th edition, 1911, 246.

[4] *Cf.* C. A. Burghardt, *Chem. News*, 1890, 61, 260; E. S. Simpson, *Ibid.*, 1909, 99, 243.

[5] *Eng. and Min. J.*, 1906, 81, 1177.

crucible with 3 to 10 g. of sodium peroxide. The fused mass is taken up with boiling water, acidified with hydrochloric acid, and the tin is determined in the solution.

Analytical methods for tin-stone and tin-pyrites are described by Fresenius.[1] Tin-stone may be treated by fusion with sodium carbonate and sulphur (H. Rose's method) but it is advisable to attack tin pyrites with aqua regia.

A.—Gravimetric Determination of Tin

1. Stannic Oxide Method.

On treating metallic tin with nitric acid, metastannic acid is formed and this reaction forms the basis of one of the methods largely used for the determination of small quantities of tin in alloys, etc.

In the absence of antimony and insoluble matter, the material may be decomposed with dilute nitric acid (sp. gr. 1·2), taken down nearly to dryness, diluted with hot water, filtered off preferably through a pulp filter, washed with 5 per cent. nitric acid, ignited strongly and weighed as SnO_2.

In solutions containing tin in the quadrivalent form, hydrated stannic oxide may be precipitated by means of an excess of ammonia, but solutions containing bivalent tin must be treated with hydrogen peroxide and then with ammonia to obtain a similar precipitate. The solution is then digested for some time to allow collection of the precipitate which is then filtered, washed, dried, ignited and weighed as SnO_2. Alkaline stannate solutions must be acidified with hydrochloric acid before adding ammonia and all metals precipitated by the latter reagent must be absent, together with oxalates, tartrates, etc., $SnO_2 \times 0{\cdot}7877 = Sn$.

2. Stannic Sulphide Method.

In the absence of other metals precipitated by sulphuretted hydrogen, this method is sometimes used. For its success the tin must be in the quadrivalent form and the solution must be free from nitric acid and other oxidising agents.

The solution should contain about 3·5 per cent. hydrochloric acid, a rapid stream of sulphuretted hydrogen passed and the solution slowly heated to 90°. The precipitate, which should settle and filter readily, is filtered, washed with ammonium nitrate solution, dried, separated from the filter paper and the latter burnt separately, the residue therefrom being moistened with nitric acid and re-ignited. The main precipitate is then added and the whole ignited, at first gently and then at a full red heat, cooled, and weighed as SnO_2.

[1] *Quantitative Analysis*, 7th edition, vol. ii., pp. 427-428.

3. Electrolytic Method.[1]

M. Heidenreich deposits the tin from a hot oxalate solution, acidified with oxalic acid, in a coppered Classen dish, and obtains in four to four and a half hours an adhesive deposit of silvery metal. To the solution (about 150 c.c.), containing about 0·3 g. of tin, 4 g. of ammonium oxalate is added, the solution acidified with 9 to 10 g. of oxalic acid, warmed to 60° to 65°, and electrolysed with a current of 1 to 1·5 ampère per 100 sq. cm. of cathode surface. The washing must be done without breaking the circuit. The dish is rinsed with water and alcohol, and dried at 80° to 90°.

In connection with the revision of the atomic weight of tin G. P. Baxter and H. W. Starkweather[2] used an electrolytic method for the exact determination of tin in stannic chloride. The solution was electrolysed in a glass vessel with platinum anode and cathode, the latter being covered with a layer of mercury and the amalgam obtained was dried and weighed.

B. VOLUMETRIC DETERMINATION OF TIN

Volumetric methods for the determination of tin are very largely used as they can be carried out much more rapidly than the gravimetric methods, and yet, with careful work, are capable of giving very good results. The following are the methods most often used:—

1. Titration of stannous chloride with iodine in acid solution.
2. Titration of stannous chloride with ferric chloride solution.

1. The Iodine Method in Acid Solution.[3]

This method is suitable for the analysis of white-metal alloys and also for the determination of tin in the solutions obtained from the treatment of the results of fusion of ores, slags, residues, etc., with sodium hydroxide, sodium peroxide, etc., the tin being readily determined by reducing the hot solution of the chloride, cooling in an atmosphere of carbon dioxide, and titrating the cold solution with iodine in the presence of starch. The solution may be conveniently reduced by means of iron[4] or nickel.[5] If antimony, arsenic, or

[1] Cf. *Quantitative Analysis by Electrolysis*, A. Classen, translated by B. Boltwood, p. 212; *Electro-Analysis*, E. F. Smith, p. 95; Heidenreich, *Ber.*, 1895, **28**, 1586; *J. Soc. Chem. Ind.*, 1896, **15**, 744; C. Engels, *Ber.*, 1895, **28**, 3187; *J. Soc. Chem. Ind.*, 1896, **15**, 219.

[2] *J. Amer. Chem. Soc.*, 1920, **42**, 905.

[3] S. W. Young, *J. Amer. Chem. Soc.*, 1897, **19**, 809; *J. Chem. Soc. Abstr.*, 1898, **74**, 192; J. D. F. Druce, *Chem. News*, 1920, **121**, 173.

[4] Parry, *Assay of Tin and Antimony*, 1904, p. 23.

[5] Beringer, *Text-book of Assaying*, 15th edition, 1921, p. 288; *cf.* R. L. Hallett, *J. Soc. Chem. Ind.*, 1916, **35**, 1087.

copper are present, they will be precipitated, and will not interfere under the conditions of the assay. A modification of the method consists in reducing the stannic chloride with finely divided metallic antimony.[1] The reduction of 0·15 g. of tin is complete after one minute's boiling, and the excess of antimony which remains undissolved acts as a safeguard during the cooling, since it reduces any tin which may have become oxidised whilst the solution is still hot. Cold solutions of stannous chloride oxidise less readily. The presence of iron, chromium, nickel, cobalt, zinc, manganese, aluminium, bismuth, phosphorus, and sulphur is without effect on the results. Copper is reduced to cuprous chloride, and if the iodine is added in drops to the vigorously agitated solution, so as to prevent the formation of a local excess of iodine, accurate results may be obtained. Lead is without effect if sufficient hydrochloric is present to prevent the formation of lead iodide. Mercury is reduced to the metallic state, but is not oxidised in cold solutions. If molybdenum or tungsten is present, a coloured lower oxide is formed, which interferes with the end reaction; these metals should, therefore, be separated. Arsenic interferes seriously if more than one part in two hundred parts of tin is present.

The following method is adopted when the reduction is effected with antimony. One gram of the alloy is dissolved in hydrochloric acid with addition of potassium chlorate, the chlorine boiled off, and the solution diluted to 100 c.c. An aliquot portion of the solution, which contains about 0·15 g. tin, is measured out and run into a flask; this is diluted to about 150 c.c. with water containing one-fifth of its volume of hydrochloric acid, heated, a little finely powdered antimony added, and the whole boiled. The flask may be fitted with a rubber cork and leading tube. After boiling for a minute or two, the solution is cooled, starch added, and the liquid titrated with the standard iodine solution.

The reduction by means of iron (Parry) is carried out as follows:—Half to one gram of the finely divided alloy is dissolved in hydrochloric acid with the addition of potassium chlorate to aid solution; after dilution, the chlorine is boiled off and a clean piece of iron rod is placed in the solution, resting against the side of the beaker, which is covered with a watch-glass. The whole is heated to 80° to 90° for twenty to thirty minutes after the solution has become colourless. The solution is cooled, and when cold the watch-glass and iron rod are washed rapidly with a little cold, boiled water, starch added, and the solution titrated rapidly with iodine. It is not necessary to remove the precipitate of antimony, arsenic, and copper. The volume of the solution should not exceed 50 c.c., the quantity of hydrochloric

[1] Ibbotson and Brearly, *Chem. News*, 1901, **84**, 167.

acid being about one-fifth of the total volume, and the amount of tin present not more than 0·5 g.

Metallic nickel[1] is largely used for reducing the stannic chloride solution, nickel foil in strips about 20 cm. long and 5 cm. wide being coiled upon itself to form a cylinder. The prepared coils are conveniently inserted in the solution to be reduced by threading on a glass rod on the end of which a knob has been pressed; by this means the coils can be withdrawn readily at the proper time. The nickel coil should be inserted into the solution when the latter is just on the point of boiling and left in for about thirty minutes after the solution becomes colourless. Coils which appear to be passive may generally be improved by boiling for a short period in hydrochloric acid.

The iodine solution is made by dissolving 11 g. of iodine and 22 g. of pure potassium iodide in a little water, and diluting to 1 litre.

The iodine solution may be standardised with pure tin or As_2O_3; the latter gives less reliable results than the former.

2. The Ferric Chloride Method.

When ferric chloride is added to a concentrated, hot hydrochloric acid solution of stannous chloride, it is immediately reduced to ferrous chloride, stannic chloride being produced at the same time. One drop in excess of the ferric chloride serves to indicate the end-point by giving a decided yellow colour to the previously colourless solution, the colour being more marked the hotter and the more strongly acid the solution remains. The presence of chlorides of lead, zinc, aluminium, ferrous iron, cobalt, nickel, antimony (antimonic), copper (cuprous), and cadmium, does not interfere with the process. Large quantities of cobalt chloride and nickel chloride give highly coloured solutions which render the recognition of the end-point difficult, but this may be overcome to some extent by diluting the solution with hot water. Bismuth chloride and mercuric chloride are reduced to metal by stannous chloride, and must, therefore, be removed by separation with iron. Precipitated antimony, copper, arsenic, and the blue oxide of tungsten are attacked by the hot acid solution of ferric chloride, and must not be present; titanium must also be absent.

The standard solution, which must be free from nitric acid and arsenic, is made up either from pure iron or by dissolving 150 g. of ferric chloride in water, adding 300 to 500 c.c. of hydrochloric acid, and diluting to 2 litres. It is standardised by dissolving 1 g. of pure tin

[1] *Cf.* R. H. Hallett, *J. Soc. Chem. Ind.*, 1916, 35, 1087.

in 200 c.c. of concentrated hydrochloric acid in a 250 c.c. flask fitted with a rubber cork and bent glass tube leading into water, to prevent oxidation. This is boiled until solution is complete and the solution titrated at once.

With alloys containing tin, lead, zinc, aluminium, iron, cobalt, and nickel, which are soluble in hydrochloric acid, but not containing antimony, arsenic, and copper, the determination is carried out as follows:—One gram of the finely divided alloy is weighed into a 250 c.c. flask fitted with a rubber cork and leading tube, 180 c.c. of pure hydrochloric acid added, and the flask heated on a sand-bath but not boiled too rapidly, or the acid becomes too dilute before it has had time to attack the metal thoroughly; nor should it come to the boil too slowly, as in this case the metal may be completely attacked whilst there is still air in the flask, with the formation of stannic chloride. When solution is complete, the resulting liquid is titrated directly with the ferric chloride solution.

With alloys containing tin, lead, antimony, and but little copper and arsenic, 1 g. of the finely divided alloy is boiled with 50 to 75 c.c. of hydrochloric acid until action ceases; solution is completed by the cautious addition of a saturated solution of potassium chlorate. The excess of chlorine is boiled off and the solution reduced by the addition of piano wire. The action in the hot solution is rapid—arsenic, antimony, and copper being precipitated; one minute after the solution turns colourless, a thin strip of copper foil is added. When a freshly added strip of copper remains bright for one or two minutes, the solution is diluted with 50 to 60 c.c. of hot, boiled water and filtered rapidly into another flask, the precipitate being kept as far as possible out of contact with the air. The flask and paper are washed once with hot dilute hydrochloric acid. Excess of strip zinc is added to the solution to precipitate the tin, and when all action has ceased, a little of the liquid is poured into a beaker containing sulphuretted hydrogen water; a white precipitate indicates that all the tin is precipitated. The solution is poured off from the precipitated tin as completely as possible after any floating particles have been allowed to settle, and the remaining metal is dissolved in 180 c.c. of hydrochloric acid in a flask as before; the resulting solution is then titrated.

This method may be used for the determination of tin in solutions obtained from any material, by first separating the metals precipitated by sulphuretted hydrogen in a hydrochloric acid solution, dissolving the precipitate in hydrochloric acid with the addition of potassium chlorate, and treating the solution as above with iron wire and metallic zinc.

III.—Analysis of Commercial Tin, Alloys, etc.

1. Analysis of Tin.

Determination of Tin.—The tin present may be determined direct by the careful application of the iodine method given on p. 260.

Determination of Arsenic.—Ten grams of the metal, in small pieces, is dissolved in 50 c.c. of ordinary hydrochloric acid with the addition of a little potassium chlorate, the solution cooled, one-third of its volume of fuming hydrochloric acid added, and sulphuretted hydrogen passed in for a long time. The arsenic sulphide is filtered off on an asbestos filter, and washed first with hydrochloric acid, then with boiled water. It is dissolved in ammonia, the solution evaporated in a porcelain dish, the residue dissolved in strong nitric acid, and the arsenic precipitated in a beaker by magnesia mixture, ammonia, and alcohol as ammonium magnesium arsenate. This is weighed either as pyroarsenate or converted into silver arsenate (*cf.* Arsenic, pp. 274 *et seq.*).

For the determination of arsenic in tin, it is usual to distil as arsenious chloride and to titrate the distillate with iodine solution (*cf.* Arsenic in Copper, pp. 265 *et seq.*).

B. S. Evans[1] converts the arsenic to hydrogen arsenide in the usual way by the Marsh test, but passes the gas over a roll of red hot copper which retains the arsenic; the increase in the weight of the copper gives the amount of arsenic. The results obtained, however, are uniformly low to the extent of 1·4 per cent.

Determination of Lead, Copper, and Iron.—Ten grams of the metal is dissolved in the smallest possible quantity of hydrochloric acid with the addition of a few crystals of potassium chlorate. Thirty grams of tartaric acid (specially tested for lead) is then added as ammonium tartrate, the solution cooled, saturated with ammonia, sulphuretted hydrogen water added, drop by drop, till no more precipitate is formed, and after gently warming on the water bath, the sulphides of copper, lead, and iron filtered off. The sulphides, after washing with very dilute sulphuretted hydrogen water, slightly acidified with sulphuric acid, are dissolved in hot nitric acid, the solution transferred to a porcelain dish, the filter ash added, evaporated on the water bath with a slight excess of sulphuric acid, the residue heated on a sand bath till fumes of sulphuric acid begin to be evolved, allowed to cool, taken up with a little water, and the lead sulphate, which usually contains a trace of tin, filtered off. After weighing the impure lead sulphate, it is extracted by warming with a solution of ammonium acetate, the lead again precipitated by sulphuretted hydrogen and converted into pure lead sulphate. In the acid filtrate from the impure

[1] *Analyst*, 1920, 45, 8.

lead sulphate, the copper is precipitated by sulphuretted hydrogen, and in the filtrate from the copper the iron is finally precipitated by oxidation with bromine water, and warming with excess of ammonia.

Commercial tin fairly frequently contains antimony, and is then analysed volumetrically like white-metal (see below).

2. Tin in Tinplate Residues

is determined by the methods either of Lunge and Marmier or Mastbaum, described under Iron (p. 84).

3. Tin Alloys.

White-metals (antifriction metals), britannia metal, solders and similar alloys of tin with antimony, lead, and copper.

(*a*) The individual metals present are frequently determined on separate weighings,[1] volumetric methods being used when available. The following are the details for the determination of tin:—From 0·5 to 1 g. of the finely divided sample is dissolved in strong hydrochloric acid, if necessary with the aid of a few crystals of potassium chlorate. After solution is complete, water is added and the stannic chloride solution thus obtained is reduced by means of iron or nickel, cooled in a current of carbon dioxide and titrated with standard iodine solution in the presence of starch (*cf.* p. 260).

W. B. Vietz[2] describes a method for the determination of copper, tin, and antimony on one weighing. The sample is dissolved in strong sulphuric acid, and the copper determined colorimetrically, the solution is diluted, 10 c.c. hydrochloric acid added, and antimony determined by titration with permanganate, after which 1 g. of powdered antimony and 25 to 50 c.c. hydrochloric acid are added, the tin reduced by boiling for a few minutes in a current of carbon dioxide, the solution then cooled and titrated with iodine in the presence of starch.

A rapid method for the determination of arsenic, antimony and tin somewhat similar to the above is given by F. A. Stief.[3] In this method 0·5 g. of the sample is dissolved in 8 c.c. concentrated sulphuric acid, the solution cooled, diluted slightly, a little pumice stone, and then 20 c.c. hydrochloric acid added and distilled at 107° for ten to fifteen minutes. The distillate is condensed in a special S-shaped condenser, and is used for the determination of arsenic by titration with iodine. The main solution is used for the determination of antimony and tin as above.

If distillation is conducted at a somewhat higher temperature in

[1] *Cf.* E. W. Hagmaier, *Chem. and Met. Eng.*, 1917, **16**, 84.
[2] *Metal Ind.*, 1910, **2**, 269.
[3] *Ind. Eng. Chem.*, 1915, **7**, 211.

order to ensure that all the arsenic is driven over, the distillate is liable to be contaminated with antimony; titration with bromate should then be used. The first titration gives arsenic plus antimony, after which the solution is boiled down in the presence of sodium sulphite and titrated a second time, giving antimony only which is deducted from the gross arsenic value (*cf.* p. 238).

(*b*) When a complete separation and examination is desired on one weighing, the following method may be used :—One gram of the finely divided metal is dissolved, without heating, in 15 c.c. of fuming hydrochloric acid with the addition of strong nitric acid (sp. gr. 1·4), drop by drop. Alloys containing 80 per cent. and over of lead are treated with aqua regia (prepared from dilute acids, 30 c.c. for 1 g. of metal) in the form of very fine turnings and gently warmed for a long time on the water bath. Nitric acid is then added until the solution becomes distinctly yellow, or if copper is present until the colour is yellowish green; aqua regia, previously warmed until chlorine begins to be evolved, is also suitable for dissolving the alloy. To the solution so obtained, ten times its volume of absolute alcohol is added in small quantities at a time, thereby precipitating lead chloride in large, easily filtered crystals; only about 1 mg. of lead remains in solution as chloride. The lead chloride is then washed carefully with alcohol, and as little as possible brought on to the filter paper. After drying, the lead chloride is shaken into a large weighed crucible, any adhering to the glass washed with hot water into the crucible, the filter paper washed with hot water, the combined solutions evaporated on the water bath, the residue dried in the air bath at 150° for three hours, and the lead chloride weighed. $PbCl_2 \times 0{\cdot}7450 = Pb$.

The alcohol in the filtrate from the lead chloride is driven off by evaporation, 1 g. of tartaric acid as ammonium tartrate added, the solution made distinctly ammoniacal, sulphuretted hydrogen water added in small quantities until no further precipitate is formed, when warming on the water bath causes the precipitate (consisting of sulphides of copper, bismuth and mercury, and traces of sulphides of lead and iron) to coalesce. This precipitate is filtered off, washed with sulphuretted hydrogen water; hot dilute nitric acid is poured over the filter paper and the copper and bismuth determined in the solution thus obtained. This is carried out by evaporating to a small bulk, diluting with water, adding ammonia until neutralisation is complete, rendering faintly acid with hydrochloric acid and digesting for about one hour. The whole of the bismuth is then precipitated as oxychloride and may be filtered off and weighed as such (*cf.* p. 247). The copper is then determined in the filtrate by one of the usual methods. The residue from the treatment of the mixed sulphide precipitate with nitric acid contains the mercury (if present) as sulphide, and this is dissolved in

aqua regia and precipitated as mercurous chloride by the addition of phosphorous acid. It is filtered on to a weighed filter paper, dried, and weighed as mercurous chloride. $Hg_2Cl_2 \times 0{\cdot}8493 = Hg$.

After acidifying the filtrate from copper, bismuth, etc., with hydrochloric acid, tin and antimony are precipitated as sulphides by sulphuretted hydrogen.

The mixture of tin and antimony sulphides is dissolved in hydrochloric acid and potassium chlorate, the solution transferred to a porcelain dish, diluted with a little water and the antimony precipitated by Tookey's method, which consists of digesting on a water bath with pure iron. (The preparation of pure iron for this purpose is as follows:—A dilute solution of ferrous chloride is precipitated with oxalic acid, the yellow oxalate completely washed by decantation with water, dried, converted into ferric oxide by ignition in a muffle and then reduced by heating strongly in a porcelain tube in a current of pure hydrogen. The spongy iron so obtained is specially suitable for the separation of antimony from tin.) If perfectly pure iron is not obtainable, iron or steel turnings free from copper, or piano wire may be used. The precipitation is complete in about thirty minutes, after which the solution is further warmed until only a little iron is left undissolved, the antimony filtered off on to a paper on which a few centigrams of iron are placed and then washed with boiled water strongly acidified with hydrochloric acid. The antimony, associated with iron, is dissolved in hydrochloric acid and a little potassium chlorate, the solution is diluted and boiled, and the antimony reprecipitated by sulphuretted hydrogen. The antimony sulphide, which always contains some chloride, is dissolved in ammonium sulphide, reprecipitated by warming with dilute sulphuric acid or acetic acid, washed off the filter paper into a dish, and evaporated to dryness on the water bath. The antimony sulphide adhering to the filter paper is dissolved off in ammonium sulphide, the solution allowed to run into the dish, again evaporated, the dish removed from the water bath, covered with a clock glass, and fuming nitric acid run on to the residue from a pipette. The antimony sulphide is immediately oxidised without separation of sulphur, and after warming for a short time the contents of the dish are washed with a little water into a weighed porcelain crucible, evaporated, the sulphuric acid driven off on a sand bath, the residue strongly ignited and weighed as oxide. $Sb_2O_4 \times 0{\cdot}7920 = Sb$.

The filtrate from the metallic antimony is nearly neutralised with ammonia, diluted, and the tin precipitated by passing in sulphuretted hydrogen. The dark brown stannous sulphide is then filtered off, washed with dilute sulphuretted hydrogen water containing a few grams of ammonium sulphate, dried and converted into stannic oxide

by ignition in a porcelain crucible. After igniting for some time, a small piece of ammonium carbonate is added to the crucible, the lid replaced and the whole again ignited strongly in order to obtain the stannic oxide free from sulphuric acid. $SnO_2 \times 0{\cdot}7877 = Sn$.

In these alloys, arsenic (from the commercial antimony) is generally found only in traces. If it is to be determined, a separate sample of several grams is dissolved in hydrochloric acid and potassium chlorate, any separated lead chloride filtered off, strong hydrochloric acid added, sulphuretted hydrogen passed in, and the copper sulphide, together with arsenic sulphide as impurity, filtered through an asbestos filter. After washing with hot water, the small amount of arsenic sulphide is dissolved out with hot ammonia, the solution evaporated in a porcelain dish, oxidised with strong nitric acid, and the arsenic precipitated as ammonium magnesium arsenate. The trace of copper which is dissolved remains unprecipitated in the ammoniacal solution.

(*c*) *Alloys containing less than 15 per cent. of Lead and Copper.*—One g. of the alloy rich in tin is dissolved in hydrochloric acid and potassium chlorate, 13 g. of tartaric acid as ammonium tartrate added, the diluted solution saturated with ammonia, and the copper and lead then precipitated by careful addition of sulphuretted hydrogen water; the further treatment of the precipitate is carried out as described on p. 264. Iron and possibly zinc are found in the precipitate. Tin and antimony are precipitated in the filtrate by acidifying with hydrochloric acid and passing sulphuretted hydrogen, and are separated by means of iron, etc., as given above.

(*d*) *Alloys free from Lead* (H. Nissenson and F. Crotogino[1]).—Half a gram of the alloy, as finely divided as possible, is placed in an Erlenmeyer flask of 200 to 300 c.c. capacity, about 7 c.c. of concentrated sulphuric acid poured on and heated, till the evolution of gas ceases and the alloy is dissolved, which takes but a few minutes. The solution is cooled and carefully diluted with hot water, and the yellow precipitate, which forms immediately, allowed to settle whilst hot. This contains both tin and antimony, the latter as an antimonious salt. On oxidation, preferably by means of ammonium persulphate, the precipitate is rendered more easy to filter, but even without this it is still easier to deal with than when oxidised by means of nitric acid. After washing, which may be neglected if other metals are not present, the paper and precipitate are ignited and the mixture of tin and antimony oxides weighed after strong ignition. The filtrate is tested for iron cadmium, zinc, etc.

A second sample of 0·5 g. is dissolved in sulphuric acid, cooled, a little hot water added, then 15 c.c. of dilute hydrochloric acid, and the antimony precipitated with iron wire; the precipitation is complete

[1] *Chem. Zeit.*, 1902, 26, 984; *J. Soc. Chem. Ind.*, 1902, 21, 1350.

in a very short time. The separated antimony and copper is dissolved in hydrochloric acid and a few drops of nitric acid, precipitated with sulphuretted hydrogen, and the antimony sulphide dissolved in sodium sulphide and the solution electrolysed. The sulphides remaining undissolved may then be dissolved in nitric acid and tested for copper, bismuth, etc.

(*e*) *Alloys containing Lead* (H. Nissenson and F. Crotogino [1]).—If only tin and lead are to be determined, the alloy is treated by warming on the sand-bath or over a free flame with concentrated sulphuric acid, which acts the more easily the higher the content of tin and antimony and the smaller the amount of copper present, the contents of the flask cooled, treated with some hot water and a considerable quantity of ammonium oxalate, allowed to cool slowly, and the precipitate of lead sulphate filtered off. The tin is determined in the filtrate by electrolysing the hot solution diluted to 180 c.c.

The determination of lead in alloys containing tin and antimony offers many difficulties and the following method is given by A. G. Blakeley and E. M. Chance [2] with a view of eliminating them. The solution of the alloy in hydrochloric acid to which potassium chlorate has been added, is evaporated to a pasty consistency, then water and tartaric acid are added, followed by sodium hydroxide and sodium hydrosulphide. The precipitate is filtered off, washed and dissolved in nitric acid, sulphuric acid added and the solution evaporated to fumes. After cooling, powdered permanganate is added and the flask and contents re-heated. The whole is again cooled, water added, the solution boiled and sulphurous acid added until the pink permanganate colour is discharged. The solution is cooled again, after which alcohol is added and the lead sulphate filtered off, washed with dilute sulphuric acid and either weighed or determined volumetrically after solution in ammonium acetate.

The following method is used with considerable success in the Department of Metallurgy, Sir John Cass Technical Institute, London:—Antimony is determined volumetrically by the bromate or permanganate method, the solution from the former being reserved for a copper determination. Tin is also determined volumetrically by the iodine method, a separate sample being used. The determination of arsenic is made in accordance with the distillation method previously described (p. 205). In the determination of lead, iron, zinc and copper, 0·5 g. of the alloy is transferred to a beaker, 10 g. of tartaric acid and 15 c.c. of water added, the whole is warmed, and when the acid is dissolved, the alloy is dissolved by means of dilute nitric acid (1 to 1), a few drops being added at a time until the total added is 10 c.c. During this stage the solution is kept nearly at boiling point. A

[1] *Loc. cit.* [2] *J. Soc. Chem. Ind.*, 1911, **30**, 518.

solution of dilute sulphuric acid is now prepared by adding 5 c.c. of concentrated acid to 30 c.c. water and this is poured into the lead nitrate solution. After cooling to room temperature, lead sulphate is filtered off and determined gravimetrically or volumetrically by titration with ammonium molybdate solution. The filtrate and washings from the lead sulphate precipitate, after nearly neutralising with sodium hydroxide solution, are run in rapid drops from a separating funnel into a hot solution of sodium hydroxide (20 g. in 300 c.c. water), after which, iron, zinc, and copper are precipitated by the passage of sulphuretted hydrogen through the alkaline solution. After filtering off and washing, the mixed sulphide precipitate is dissolved in nitric acid, the solution evaporated to fumes after the addition of a small quantity of sulphuric acid and eventually copper is precipitated by means of sulphuretted hydrogen. The filtrate and washings from the copper sulphide precipitate are treated in the usual way for separation and determination of iron and zinc.

4. Phosphor-Tin.

This alloy usually contains 4 to 5 per cent. of phosphorus (occasionally up to 10 per cent.) and comes into commerce in dark grey blocks which show a crystalline fracture; it is used in the manufacture of phosphor-bronze.

For the analysis, 0·5 g. of fine borings are covered in a large beaker with 15 c.c. of fuming hydrochloric acid in which a large quantity of potassium chlorate has been dissolved by shaking in the cold. The contents of the beaker are swirled round, and, after addition of some more solid potassium chlorate, gently warmed, diluted to 200 c.c., all the tin precipitated as sulphide by passing in sulphuretted hydrogen for a long time, the beaker placed on a water bath (95° to 100°) for half an hour, the tin sulphide filtered off and washed with very dilute sulphuretted hydrogen water, to which ammonium acetate and acetic acid are added. The dried sulphide is removed as completely as possible from the paper, the paper ignited in a weighed porcelain crucible, the sulphide added, heated with a small flame, then more strongly, and finally ignited, after the addition of a small piece of ammonium carbonate. The stannic oxide so obtained is weighed. The filtrate is evaporated down to about 30 c.c., and after the addition of magnesia mixture, saturated with ammonia. After six hours the ammonium magnesium phosphate is filtered off, washed with dilute ammonia (1 : 2), dried and removed from the filter paper; the portion that remains adhering to the paper is dissolved off in warm, dilute nitric acid, the solution evaporated in a weighed porcelain crucible, the dry ammonium magnesium

phosphate added, very slowly heated over a Bunsen burner, and finally ignited over the blowpipe, the lid being placed on for the final strong ignition. The magnesium pyrophosphate so obtained is weighed. $Mg_2P_2O_7 \times 0{\cdot}2785 = P$.

J. Arnott[1] recommends that for the determination of phosphorus 2 g. be taken, dissolved in hydrochloric acid and ferrous sulphate, the resulting solution boiled until free from fumes, cooled, made alkaline with ammonia and then acidified with nitric acid. This solution is then made up to a definite bulk and the phosphorus precipitated with ammonium molybdate solution on a portion equivalent to 0·05 g. of alloy.

Gemmel and Archbutt[2] use a gas evolution method followed by a precipitation of the phosphorus as magnesium pyrophosphate. A suitable weight of alloy is attacked with concentrated hydrochloric acid and the phosphine evolved led to absorption bottles or flasks containing bromine and bromine water.

Volumetric methods for the analysis of phosphor-tin have been worked out by R. E. Lee, A. H. Fezeley and F. H. Reichel,[3] who dissolve a suitable weight of the alloy in hydrochloric acid in the first of a series of connected flasks, using a non-oxidising atmosphere of coal-gas or carbon dioxide. The tin dissolves as stannous chloride and the phosphorus is liberated as phosphine which is absorbed in a solution of potassium permanganate (2 g. per litre with 10 per cent. nitric acid in addition). After solution is complete the tin is determined direct by titration with iodine or ferric chloride and the phosphorus is precipitated from the contents of the absorption flasks as ammonium phosphomolybdate which may be dried and weighed or reduced and titrated in the usual way.

5. Tin Waste and Ashes.

The ashes and waste produced by tinning iron (in the manufacture of tinplate), copper, brass, and bronze by dipping in the molten metal, contain a quantity of tin (as stannous and stannic compounds and metal), as well as iron and copper oxides mixed with coke and sal-ammoniac, and are included under this heading.

L. Rürup[4] recommends Kerl's method[5] for the analysis. An average sample of 500 g. weight is mixed intimately with 100 g. of tartaric acid, 400 g. of sodium carbonate, and 60 g. of chalk in a correspondingly large Hessian crucible, a covering of sodium carbonate and

[1] *Metal Ind.*, 1920, **16**, 386. [2] *J. Soc. Chem. Ind.*, 1908, **27**, 427.
[3] *Ind. and Eng. Chem.*, 1917, **9**, 663.
[4] *Chem. Zeit.*, 1896, **20**, 406 ; *J. Chem. Soc. Abstr.*, 1897, **72**, 234.
[5] *Metallurgische Probierkunst*, 2nd ed., p. 482.

100 g. of borax added, the crucible placed in a coke fire in a wind-furnace with a good draught, and the covering brought to a limpid fluid condition in half an hour or longer. The crucible is then removed from the fire, and cooled by means of an air blast for twenty minutes, or until it has sufficiently cooled to be completely cooled by placing in water. The crucible is then broken and the metallic button cleared from slag and weighed. The button is then drilled in several places, 1 g. of the drillings taken, decomposed with nitric acid (*cf.* Analysis of Bronze, p. 216), the stannic acid separated, the filtrate evaporated with sulphuric acid, and the copper separated electrolytically. The dried stannic acid is ignited and weighed.

W. Witter takes proportional quantities of the coarse and fine products from the crushing and sieving of a representative sample of tin ashes and waste, to give an average sample of 25 g., mixes with 5 per cent. of powdered charcoal and potassium cyanide (from 50 to 100 g.), and fuses the mixture in a crucible in a wind-furnace. Drillings of the weighed button are taken and the content of tin determined either by gravimetric or volumetric methods.

6. Tin Dross.

This consists of very impure tin resulting from the prolonged use of tin for tinning copper, etc., by immersion in the molten metal, and contains copper, zinc, iron, etc. On renewal of the bath this alloy is ladled off and run into ingots.

For the analysis, several ingots are drilled through, and a 1 g. sample analysed in the same way as bronze; a somewhat high content of iron oxide in the ignited stannic acid is recognised by a brown coloration and if necessary this impurity may be determined by fusion of the stannic oxide with sodium carbonate and sulphur mixture.

7. Tin Slags.

W. Witter fuses 1 g. of the very finely ground slag with 5 g. of sodium hydroxide in a nickel crucible, dissolves the melt in water, acidifies the solution with hydrochloric acid, precipitates the tin by sulphuretted hydrogen, filters off the sulphide, washes it, dissolves it in ammonium sulphide, filters, etc., and finally weighs the stannic acid obtained. If the slag contains antimony, the separation from tin is carried out by means of iron according to Tookey-Clark's method (p. 267). After dissolving the melt in water and acidifying with hydrochloric acid, the solution may be reduced with iron or nickel and titrated with iodine (*cf.* volumetric methods, p. 260).

ARSENIC

Only a very small proportion of the compounds of arsenic which find their way into commerce are obtained directly from ores of arsenic; by far the greater quantities are obtained as by-products from the crude arsenic trioxide (white arsenic) recovered from the flues in roasting ores containing arsenic.

Arsenic Ores proper include:—

Native Arsenic (*Flaky Arsenic*), often containing antimony and silver, as well as a little iron, less frequently nickel and cobalt.

Arsenical Pyrites (*Mispickel*), $FeS_2 + FeAs_2$, with 46 per cent. of arsenic, 34·4 per cent. of iron, and 19·6 per cent. of sulphur. Frequently found together with tin-stone, iron pyrites, copper pyrites, galena, zinc blende, fahl ore, etc.

Arsenical Iron (*Leucopyrite*), $FeAs_2$, with 72·8 per cent. of arsenic, and *Löllingite*, Fe_2As_3, with 66·8 per cent. of arsenic; not infrequently containing some gold.

The natural sulphides of arsenic—*Realgar*, AsS, and *Orpiment*, As_2S_3—are used as found.

Arsenic is also found in many other ores, such as speiss cobalt, kupfernickel, etc., from which it is partially recovered by metallurgical treatment.

The products most frequently met with in analysis are:—Ores of arsenic, metallic arsenic, white arsenic, and red and yellow arsenic sulphides.

Dry Assay of Arsenic.[1]—This is employed for determining the available quantity of arsenic, arsenious acid, or sulphur compounds of arsenic in ores.

I.—Gravimetric Methods of Analysis

Arsenic is determined either as trisulphide (As_2S_3), pentasulphide (As_2S_5), magnesium pyroarsenate ($Mg_2As_2O_7$), or as silver arsenate (Ag_3AsO_4). The determination as hydrated ammonium magnesium arsenate cannot be recommended.

1. Determination as Trisulphide, As_2S_3.

The arsenic may be separated from solutions of arsenious acid (*e.g.*, in hydrochloric acid) as trisulphide, provided no substances are present which oxidise sulphuretted hydrogen. Such a solution is obtained, for instance, by distilling the arsenic as arsenious chloride (*cf.* Vol. I., p. 378,

[1] *Cf.* C. and J. J. Beringer, *Text-book of Assaying*, 15th ed., 1921, p. 382; Rhead and Sexton, *Assaying and Metallurgical Analysis*, 1914; Kerl, *Probierbuch*, 3rd ed., p. 170.

and this vol., p. 205), and condensing the distillate (arsenious chloride and hydrochloric acid) in water free from air. By carefully passing in sulphuretted hydrogen all the arsenic is precipitated as trisulphide; any traces of admixed sulphur may be extracted by means of hot alcohol, after collecting the precipitate on a filter paper dried at 100°, and washing with water. The precipitate and paper are dried at 100° to 110° till constant, and weighed. $As_2S_3 \times 0{\cdot}6092 = As$.

2. Determination as Pentasulphide, As_2S_5.

Arsenic is determined as pentasulphide when to the solution of the mixed sulphides (*cf.* separation from tin and antimony, p. 288) in hydrochloric acid and potassium chlorate, a large quantity of strong hydrochloric acid is added, and sulphuretted hydrogen passed in for a long time in the cold. It is collected on a dried asbestos filter in a Gooch crucible, washed first with strong hydrochloric acid containing sulphuretted hydrogen, then with boiling water, and finally with hot absolute alcohol, and weighed, after drying at 100° to 110°, till constant. $As_2S_5 \times 0{\cdot}4832 = As$.

F. Neher[1] recommends the use of a solution containing one volume of water and two volumes of fuming hydrochloric acid of sp. gr. 1·2, in the separation of arsenic from antimony, bismuth, lead, etc.; more hydrochloric acid retards the precipitation, which is usually completed by a rapid current of sulphuretted hydrogen in one hour. Warming must be avoided; in fact, after the addition of the strong hydrochloric acid, it is well to cool. If the solution, after standing corked in a flask for two hours, still smells strongly of sulphuretted hydrogen, one may be certain that the precipitation is complete. This method of determination was first published by Le Roy W. M'Cay.[2]

In presence of stannic chloride, a compound containing tin, which is quite insoluble in hydrochloric acid, separates with the arsenic pentasulphide.

Both the trisulphide and the pentasulphide of arsenic may be dissolved off the filter paper by pouring on a warmed mixture of ammonia and hydrogen peroxide; in the cooled solution the arsenic acid is precipitated as usual with magnesia mixture, ammonia, and alcohol.

3. Determination as Magnesium Pyroarsenate, $Mg_2As_2O_7$.

Arsenic is frequently precipitated and (in presence of tartaric acid) also separated from antimony and tin as this compound. The sulphides of arsenic, antimony, and tin are dissolved by gently warming with hydrochloric acid and potassium chlorate (the sulphides of arsenic are treated with fuming nitric acid), and the temperature raised, but not

[1] *Z. anal. Chem.*, 1893, **32**, 45; *J. Chem. Soc. Abstr.*, 1893, **64**, 186.
[2] *Chem. News*, 1886, **54**, 287.

sufficiently to melt the nearly white undissolved sulphur. If antimony and tin are present, some tartaric acid is added to the solution, which is then somewhat diluted, filtered through a small paper into a beaker, and the paper washed with a little water.

Sufficient magnesia mixture (prepared by dissolving 110 parts of crystallised magnesium chloride and 140 parts of ammonium chloride in 1300 parts of water and 700 parts of strong ammonia) is then added, the solution saturated with ammonia, one-quarter of the volume of absolute alcohol added, swirled round and allowed to stand covered, under a bell jar, for forty-eight hours. At the expense of accuracy, but without introducing any appreciable error, the precipitate may be filtered off after six to twelve hours and washed with a mixture of two volumes of strong ammonia with two volumes of water and one volume of alcohol. The precipitate and paper are dried in an air-bath, the precipitate removed as completely as possible on to glazed paper, the paper replaced in the funnel, hot, dilute nitric acid poured over it, the solution evaporated in a weighed porcelain crucible, the precipitate then introduced into the crucible, the lid placed on, the contents gently heated to drive off the ammonia and water, and the temperature gradually increased up to a dull red heat; the lid is then removed, and the crucible and its contents strongly ignited by means of a blowpipe or large Bunsen burner. If the crucible is ignited with the lid on, a considerable amount of arsenic may be volatilised owing to reduction by means of the burner gases. The crucible, whilst still hot, above 100°, is placed in a desiccator containing sulphuric acid and weighed when cold with the lid. $Mg_2As_2O_7 \times 0{\cdot}4827 = As$.

4. Determination as Silver Arsenate,[1] Ag_3AsO_4.

If a solution of arsenic acid, free from chlorides, is nearly neutralised with ammonia, silver nitrate solution added, and then just neutralised with ammonia, a chocolate-brown precipitate of silver arsenate is produced, which settles well on warming. The precipitate is washed by decantation, collected on a weighed filter paper, dried at 100° till constant, and weighed. $Ag_3AsO_4 \times 0{\cdot}1621 = As$.

The weight of the arsenate may also be determined by bringing the precipitate into a weighed crucible, evaporating off the water, and drying the residue in an air-bath; it is still quicker to dissolve the washed arsenate in dilute nitric acid, add some ferric sulphate to the diluted solution, and determine the silver by titration with ammonium thiocyanate standardised against silver (Volhard's method, p. 122). $Ag \times 0{\cdot}2316 = As$. $Ag \times 0{\cdot}3058 = As_2O_3$.

A good excess of silver nitrate is used, and the filtrate from the

[1] *Cf.* W. Eschweiler and W. Röhrs, *Z. angew. Chem.*, 1923, 36, 464.

silver arsenate tested by adding a few drops of dilute ammonia, which should give no further brown coloration of silver arsenate. No silver oxide is precipitated in the slightly over-neutralised solution, since, according to Le R. W. M'Cay, it is soluble in small quantities in the solution containing ammonium nitrate.

Owing to the appreciable solubility of silver arsenate in ammonium nitrate, J. Waddell[1] considers the method unsatisfactory, and has suggested two modifications as follows:—

(1) The nitric acid solution is rendered slightly alkaline by the addition of pure sodium hydroxide then just reacidified with acetic acid before adding the silver nitrate.

(2) The silver nitrate is first added to the nitric acid solution which is afterwards neutralised with zinc oxide.

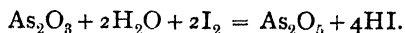
On account of the high molecular weight and small percentage of arsenic in silver arsenate, Finkener dissolves small quantities of ammonium magnesium arsenate, after drying, in dilute nitric acid, evaporates the solution in a weighed porcelain crucible, adds excess of silver nitrate, and evaporates several times with 10 to 20 c.c. of water until a fresh addition of water produces no further formation of arsenate (or darkening of the silver arsenate); the arsenate is then washed by decantation, dried, and weighed. A small amount of silver chloride as impurity in the arsenate is recognised on dissolving the weighed silver arsenate in dilute nitric acid; the silver chloride may either be collected on a small filter paper, weighed as such and deducted from the weight of the impure arsenate, or the nitric acid solution of the arsenate may be titrated as stated above.

Any chloride in the solution may be separated before neutralising with ammonia by the addition of silver nitrate and filtering off any silver chloride precipitated. Solutions containing sulphuric acid must be diluted on account of the slight solubility of silver sulphate.

II.—Volumetric Methods

1. Determination of Arsenious Acid.

The method of F. Mohr depends on the oxidation of the solution, rendered. alkaline by sodium bicarbonate, by means of iodine, in presence of starch as indicator, in accordance with the equation:—

$$As_2O_3 + 2H_2O + 2I_2 = As_2O_5 + 4HI.$$

Stannous salts and antimonious acid should not be present; solutions of these, to which Rochelle salt is added and then made alkaline with sodium bicarbonate, may likewise be titrated with iodine solution (*cf.* p. 285).

[1] *Ind. Eng. Chem.*, 1919, 11, 939.

For the preparation and standardisation of the iodine solution, *cf.* Vol. I., p. 67.

The solution to be titrated (*e.g.*, of white arsenic or flue dust, etc.) may conveniently contain 0·1 g. of arsenious oxide; it is neutralised with sodium carbonate, then 20 c.c. of a cold, saturated solution of sodium bicarbonate (prepared from the commercial salt, washed free from any adhering sodium carbonate by means of water) added, and titrated after the addition of starch solution. Alkaline solutions are first just acidified with hydrochloric acid, then sodium bicarbonate solution added, etc.

Solutions of arsenic acid are evaporated with sulphuric acid in order to drive off any nitric acid, the residue taken up with a large excess of a saturated aqueous solution of sulphur dioxide, gently warmed, the sulphur dioxide completely expelled by boiling, the solution cooled and neutralised, etc., as above.

H. Nissenson and A. Mittasch[1] titrate the arsenic and antimony together in the sulphuric acid solution of the sulphides by means of $N/10$ potassium bromate solution[2] (*cf.* Analysis of Hard Lead, p. 238), using a few drops of indigo solution as indicator. For the determination of the antimony a second sample of 1 g. is treated with brom-hydrochloric acid and heated for a considerable time in the fume cupboard in order to drive off the arsenic; after diluting with water the antimony is precipitated by sulphuretted hydrogen. The sulphide is then dissolved in 50 c.c. of a cold, saturated solution of sodium sulphide, the solution heated to boiling, filtered into a platinum dish, and after addition of boiling water electrolysed for forty minutes with a current density of about 1·6 ampères per square decimetre.

Antimony may also be determined by treating a second sample of 1 g. with brom-hydrochloric acid as above and heating until arsenic is driven off, after which 3 or 4 g. of fresh sodium sulphite crystals are added, and the solution boiled down as rapidly as possible to about 10 c.c. The solution is then diluted with 20 c.c. strong hydrochloric acid and 40 c.c. hot water, boiled for one minute and titrated hot with potassium bromate using methyl orange as an indicator (*cf.* Volumetric Determination of Antimony—Bromate Method, p. 286).

2. Determination of Arsenic Acid.

The method generally used (that of Baedeker and Brügelmann) depends on the precipitation of the arsenic acid by a solution of uranyl acetate or uranyl nitrate ($UO_2(NO_3)_2 + 6H_2O$), the end-point being recognised by means of spot tests with potassium ferrocyanide solution.

[1] *Chem. Zeit.*, 1904, **28**, 184; *J. Soc. Chem. Ind.*, 1904, **23**, 338.
[2] Györy, *Z. anal. Chem.*, 1893, **32**, 415; *J. Chem. Soc. Abstr.*, 1893, **64**, 554.

The uranium solution should contain about 20 g. of uranium oxide to the litre. For its standardisation a weighed quantity (about 0·2 g.) of arsenious oxide is dissolved in a flask by boiling with strong nitric acid, the solution evaporated, the residue dissolved in water, neutralised with sodium hydroxide or ammonia, strongly acidified with acetic acid, uranium solution run into the cold solution until the greater part of the arsenic pentoxide is precipitated, the solution heated to boiling for a few minutes, and then titrated further with the uranium solution until a red coloration is given with a drop of potassium ferrocyanide solution on a porcelain tile.

A method in which arsenic acid is determined by difference finds considerable favour in some technical laboratories. Arsenious acid is first determined by a volumetric method, and the total arsenic is determined on a separate weighing of the sample. A suitable weight is dissolved by strongly heating with 10 c.c. of concentrated sulphuric acid, cooled, diluted with water, hydrochloric acid added, and the solution titrated hot with potassium bromate.

III.—Special Methods

1. **For Ores, Speisses, Waste, etc.** (*cf.* also Vol. I., pp. 376 *et seq.*).

(*a*) One gram of the very finely ground substance is dissolved in aqua regia or in nitric and tartaric acids, the solution diluted, sulphuretted hydrogen passed in, the precipitate extracted with hot potassium sulphide solution, and the sulphides of arsenic, antimony, and tin reprecipitated by acidifying the cooled solution with dilute sulphuric acid. The mixed sulphides are dissolved in hydrochloric acid and potassium chlorate, the solution diluted, some tartaric acid added and the arsenic precipitated by addition of magnesia mixture (see p. 274), ammonia, and alcohol, and finally weighed as magnesium pyroarsenate. The antimony and tin in the filtrate may be determined as given under the analysis of White-metals (p. 265).

(*b*) *F. Reich's and T. Richter's Method* (as employed at the Freiberg metallurgical works for raw and roasted ores).—Nitric acid (sp. gr. 1·2) is poured over 0·5 to 1 g. of the substance in a large porcelain crucible, which is covered with a watch-glass and heated on a sand-bath. After the decomposition, the watch-glass is removed and the contents of the crucible evaporated on the sand-bath. Three times the weight of pure anhydrous sodium carbonate (free from chloride) and an equal quantity of nitre are then added, and the crucible heated over a burner or in a muffle till tranquil fusion ensues. The cooled melt is extracted with hot water, the solution neutralised with nitric acid, the carbon dioxide driven off by warming, silver nitrate added, and then ammonia in very

slight excess, which precipitates the arsenic acid as silver arsenate (according to the method on p. 275). The dried precipitate is removed from the paper, the paper ignited on a scorifying dish, the precipitate together with 10 to 20 g. of assay lead added, scorified, and the lead button obtained cupelled on a cupel (*cf.* Silver Assay by Scorification, p. 102). From the weight of the silver bead obtained the amount of arsenic contained in the original substance may be calculated. One hundred grams of silver correspond to 23·17 g. of arsenic, or 30·58 g. As_2O_3.

Pearce boils the aqueous solution of the melt, acidified with nitric acid, neutralises after cooling with ammonia, filters off any precipitated aluminium compounds, precipitates the arsenic according to the method given on p. 275, dissolves the silver arsenate in dilute nitric acid, and titrates the silver by Volhard's method.

Raw ores may also be mixed with ten times their weight of a mixture of equal parts of sodium carbonate and nitre, covered with a deep layer of the same mixture, and then fused.

(*c*) Fusion of the ground ore with six times its weight of a mixture of equal parts of sodium carbonate and sulphur, and lixiviation of the melt with hot water, etc. This method is less frequently used, generally only if lead, copper or antimony, and tin are to be determined in the sample as well as arsenic.

(*d*) *Wastes* are analysed by one of the foregoing methods, or more conveniently, after evaporation of their solution in aqua regia, and addition of ferrous chloride and fuming hydrochloric acid, the arsenic is volatilised by distillation as arsenious chloride (p. 205), and the arsenic in the distillate determined by Mohr's method (p. 276).

(*e*) *F. W. Boam's*[1] *Method for the Volumetric Determination of Arsenic in Ores, etc.*—One to one and a half gram of the finely ground substance is heated with 20 to 25 c.c. of strong nitric acid, and the solution evaporated to dryness. After cooling, 30 c.c. of concentrated sodium hydroxide solution (30 per cent.) is poured on to the residue, boiled for a few minutes, some water added, filtered, and the filtrate diluted to 250 c.c. Twenty-five c.c. of this solution is acidified with 50 per cent. acetic acid in which 10 per cent. of sodium acetate is dissolved, heated to boiling, and titrated with uranium acetate solution (p. 277). Boam uses a uranium solution of which 1 c.c. corresponds to 0·00125 g. of arsenic, prepared by dissolving 17·1 g. of pure uranyl acetate in 15 c.c. of strong acetic acid and water, and then making up the solution to 2 litres.

The method is applicable to all ores decomposed by nitric acid. Any ferric arsenate formed is completely decomposed by boiling with a large excess of sodium hydroxide.

[1] *Chem. News*, 1890, 61, 219.

(*f*) *Arsenic Ores* (native arsenic, arsenical pyrites, arsenical iron) and speisses are treated according to H. Nissenson and F. Crotogino[1] by heating with concentrated sulphuric acid as follows :—Five grams of the finest possibly ground material, dried at 100°, is placed in a round-bottomed or small Erlenmeyer flask, a small funnel placed in the mouth of the flask, 15 c.c. of strong sulphuric acid poured on, and the contents heated until all metallic appearance has disappeared ; the decomposition is ended, according to the temperature, nature, and fineness of the substance, in from half to three hours. After cooling, hot water is added (by addition of cold water arsenious acid readily separates), and, after settling, the solution is filtered. The filtrate is heated to boiling, a rapid current of sulphuretted hydrogen passed in till the precipitate balls together, which generally takes place in about ten minutes, the solution filtered off into a 500 c.c. flask, and the precipitate washed well with hot water. The filtrate is boiled to expel sulphuretted hydrogen, the iron oxidised with a sufficient quantity of ammonium persulphate or hydrogen peroxide, 200 c.c. of ammonia added, and after again boiling and cooling, diluted to 500 c.c. One hundred c.c. of the solution is then filtered through a dry paper, and nickel and cobalt separated electrolytically in the usual way by diluting to about 180 c.c., and electrolysing the hot solution in a Classen dish with a current of 1 ampère per 100 sq. cm. for one to two hours, according to the amount of nickel and cobalt present. The sulphide precipitate is dissolved in hydrochloric acid and potassium chlorate, the chlorine driven off, the solution diluted to 500 c.c., 100 c.c. filtered off, neutralised with ammonia after addition of tartaric acid, and the arsenic precipitated as ammonium magnesium arsenate by means of magnesia mixture. The copper in the filtrate, if present only in very small quantity, is estimated colorimetrically ; if present in larger quantity, the filtrate is acidified with dilute sulphuric acid, the copper precipitated by boiling with sodium thiosulphate, the precipitate washed with boiling water, dried, ignited, and weighed as cupric oxide. If antimony is present, the sulphide precipitate is washed free from sulphuretted hydrogen, digested with ammonium carbonate solution to separate the arsenic, the residue extracted with 20 c.c. of concentrated sodium sulphide solution, and the antimony determined in the solution. For the determination of the copper, or bismuth and cadmium, the sulphides remaining on the filter paper are dissolved in nitric acid, etc. The treatment with concentrated sulphuric acid is especially suited for pyrites, copper pyrites, mixed zinc-lead ores, etc.

Silver in naturally occurring native arsenic is determined by scorification and cupellation (*cf.* pp. 102 and 110).

[1] *Chem. Zeit.*, 1902, **26**, 847 ; *J. Chem. Soc. Abstr.*, 1902, **82**, 695.

2. **For Sublimed Arsenic.**—This metallurgical product may contain as impurity particles of arsenical pyrites introduced during sublimation. Traces of sulphur are recognised by dissolving in aqua regia, evaporating, again evaporating with hydrochloric acid, and precipitating the hot dilute hydrochloric acid solution with barium chloride solution. Iron is determined as sulphide, FeS, by mixing a few grams of the sample with an equal weight of sulphur in a Rose's crucible, and heating gradually up to strong ignition in a current of hydrogen and then allowing the crucible to cool in the current of hydrogen.

3. **For Crude Arsenious Acid** (White Arsenic) **and Flue Dust.**—About 0·5 g. of the substance is dissolved in a flask by prolonged boiling with excess of potassium hydroxide. The solution, which is generally muddy owing to the presence of soot, sand, ferric oxide, etc., is cooled, diluted to nearly 100 c.c., and made just acid by adding hydrochloric acid, drop by drop. Fifty c.c. of a cold saturated solution of sodium bicarbonate is then added, the solution diluted to 500 c.c., in 25 c.c. of which the arsenious acid is titrated by F. Mohr's method (p. 276).

Commercial white arsenic is practically pure arsenious oxide, being contaminated only by extremely small quantities of flue dust (from the fuel of the roasting furnace) and traces of arsenic sulphide. Both are recognised by dissolving in hot hydrochloric acid, when the sulphide separates in a flocculent form. White arsenic, containing sulphur, if carefully sublimed in a porcelain dish, gives at first a reddish deposit on another dish placed over it as a cover.

White arsenic glass is nearly chemically pure arsenious oxide.

4. **For Artificially prepared Realgar** (Red Arsenic Glass) **and Orpiment** (Yellow Arsenic Glass).—The composition of these products only approximates to that of the naturally occurring sulphides, arsenic disulphide (AsS) and arsenic trisulphide (As_2S_3); for instance, yellow arsenic glass contains a considerable quantity of arsenious acid. Impurities (particles of ore, etc.) remain behind undissolved on boiling the finely ground substance with potassium hydroxide and sulphur. For the determination of the sulphur, 0·1 g. to 0·2 g. of the substance is dissolved in aqua regia and the solution further treated as described above. For the determination of the arsenic, a small portion of the sample is boiled with concentrated nitric acid, the solution diluted with water and titrated with uranium solution (p. 277). Earthy impurities remain behind when a few grams are volatilised in a crucible.

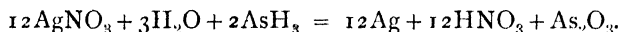
5. **In Rosaniline, Rosaniline residues, and Colouring Matters suspected of containing Arsenic.**—The arsenic is distilled as chloride, by mixing the substance with ferrous sulphate and a large quantity of common salt in a large flask, pouring on pure (arsenic free) sulphuric

acid, warming the flask on a sand-bath, and condensing the vapours in a well-cooled, spiral condenser. In rosaniline residues rich in arsenic, a small weight of the sample suffices. The arsenic in the distillate is determined by Mohr's method (p. 276).

6. In Crude Commercial Hydrochloric and Sulphuric Acids (*cf.* Vol. I., pp. 433, 519).—Acids containing arsenic evolve, when used for preparing hydrogen, in the manufacture of zinc chloride from zinc ashes, etc., corresponding quantities of the highly poisonous arseniuretted hydrogen.

For the determination of the content of arsenic, Prauss generates hydrogen from pure zinc, free from arsenic, and the diluted acid under examination. The gas is passed through a series of wash-bottles, containing a measured quantity of standard neutral silver nitrate solution, and after the experiment, the silver in the filtrate from the separated metallic silver is titrated with ammonium thiocyanate.

The decomposition of arseniuretted hydrogen takes place in accordance with the equation:—

$$12AgNO_3 + 3H_2O + 2AsH_3 = 12Ag + 12HNO_3 + As_2O_3.$$

Prauss found that the results obtained by this method are sufficiently accurate for technical purposes, *e.g.*, 0·10 per cent. instead of 0·12 per cent., as given by a gravimetric determination.

The arsenic may also be accurately determined by passing pure sulphuretted hydrogen (prepared from calcium sulphide or sodium sulphide and pure hydrochloric or sulphuric acid) for a long time into the diluted and gently warmed acid after reducing with sulphurous acid and driving off the excess; the arsenic is thus precipitated as sulphide.

7. For **Shot** (Arsenical Lead), *cf.* Lead, p. 242.

DETECTION OF ARSENIC

In many ores and metallurgical products, arsenic is contained in considerable quantities and is easily recognisable by blowpipe tests. When heated on charcoal in the blowpipe flame, a garlic-like odour is evolved, and when fused with sodium carbonate and potassium cyanide in a small glass tube sealed at one end, a dark brown metallic-looking mirror of arsenic is formed. The wet tests, such as the well-known Marsh-Berzelius test, are much more delicate; in carrying them out, only absolutely pure, specially tested reagents may be employed. These tests are fully described in Vol. I., pp. 433 *et seq.*

A sensitive test, capable of detecting 1 part of arsenic in 1,000,000 has been described by F. Feigl and F. Neuber,[1] and consists in warming

[1] *Z. anal. Chem.*, 1923, **62**, 369.

the solution containing arsenic in the pentavalent form after the addition of stannous chloride and a hydrochloric acid solution of ammonium molybdate. A blue colour indicates arsenic.

The substance to be tested for arsenic is conveniently first digested at a gentle heat with pure, 25 per cent. hydrochloric acid and some potassium chlorate, and the solution so obtained run into a simple Marsh apparatus, in which hydrogen is being evolved from pure zinc. The hydrogen is ignited and a porcelain plate held in the flame. The dark brown shiny arsenic spots disappear immediately on addition of a drop of sodium hypochlorite. In order to distinguish them from antimony spots, G. Denigés[1] dissolves them in a few drops of nitric acid, warms the solution, and then adds four to five drops of a specially prepared molybdenum solution. In the presence of 0·01 to 0·02 mg. of arsenic, some yellow ammonium arseno-molybdate is immediately formed, the regular crystals of which possess a characteristic appearance under the microscope. They are best examined in a polarisation microscope with crossed Nicols.

If pure iron (electrolytic, or reduced by hydrogen from absolutely pure ferric oxide) is introduced into a hydrochloric acid solution of antimony and arsenic, only arseniuretted hydrogen is evolved; the antimony is quantitatively separated as metal, together with a considerable quantity of arsenic. J. Thiele[2] makes use of this methed for the detection of small quantities of arsenic in presence of much antimony. Whilst 0·1 to 0·15 mg. of arsenic may be detected in an arsenic solution by means of the hydride evolved by the introduction of pure iron, the test becomes much more delicate if 2 to 3 c.c. of a concentrated solution of antimony oxychloride in hydrochloric acid of sp. gr. 1·124 is gradually run in. This procedure appears specially suited to the qualitative detection of arsenic in antimonial pharmaceutical preparations.

ANTIMONY

The metal, the liquated sulphide, Sb_2S_3, and the numerous antimonial preparations are generally prepared from *Stibnite* (grey antimony ore, Sb_2S_3), the most common ore of antimony, which contains 71·7 per cent. of antimony. Other antimony ores are :—*Antimony bloom* (Valentinite and Senarmontite), Sb_2O_3, and *Antimony ochre* (Cervantite, Sb_2O_3, Sb_2O_5, and Stiblithe, Sb_2O_3, $Sb_2O_5 + 2H_2O$). Hard lead (antimonial lead) is prepared in large quantities in metallurgical works from lead

[1] *Comptes rend.*, 1890, **111**, 824; *J. Chem. Soc. Abstr.*, 1891, **60**, 364.
[2] *Annalen*, 1891, **263**, 361; *J. Soc. Chem. Ind.*, 1891, **10**, 857.

and copper ores containing antimony; it comes on to the market with very varying content of antimony.

Analyses of the following products are most frequently required:—Ores, metallic antimony, hard lead, and other alloys rich in antimony (bearing metal, etc.). The dry assays for ores[1] are inaccurate and are now seldom used. Of the gravimetric methods, the determination of the antimony as tetroxide and the electrolytic separation of the metal from solutions of the sulpho-salt are described; as are also several volumetric methods well suited to technical purposes.

I. Gravimetric Methods of Analysis[2]

1. Determination as Antimony Tetroxide, Sb_2O_4.—The antimony sulphide obtained by precipitation with sulphuretted hydrogen, or by acidifying solutions of the sulpho-salt, is treated with strong nitric acid until all the sulphur is oxidised,[3] the excess of acid removed by evaporation, the sulphuric acid carefully driven off, and the residue strongly ignited in an uncovered porcelain crucible supported in a round hole in a stout piece of asbestos board, and finally weighed as tetroxide. For this ignition E. G. Beckett[4] considers that a muffle furnace at a temperature of 800° to 900° is essential for accurate results. $Sb_2O_4 \times 0{\cdot}7920 = Sb$.

When a few milligrams only of antimony sulphide are to be treated it is dissolved in warm ammonium sulphide, the solution evaporated in a large, weighed porcelain crucible, and the residue then oxidised with strong nitric acid. Larger quantities of precipitated antimony sulphide and sulphur are washed from the filter paper into a large dish, evaporated to dryness on the water bath, the dish covered, and the contents completely oxidised with strong nitric acid; all the sulphur is thus immediately oxidised. After warming a short time, the contents of the dish are washed into a weighed crucible, and evaporated, etc., as above. (See also analysis of bearing metal, p. 265.)

2. Electrolytic Determination.[5]—According to Classen, the deposition of the antimony is best carried out in a solution of the sulphide in a large excess of concentrated sodium sulphide solution; with a solution containing from 50 to 70 per cent. of a cold, saturated sodium sulphide solution, the current used is from 1 to 2 ampères, and the E.M.F. may vary between 1·5 and 3 volts. By warming the solution to 60° to 80°,

[1] *Cf.* Kerl, *Probierbuch*, 2nd ed., 1894.

[2] A bibliography of methods of analysis of antimony has been prepared by E. R. Darling, *Chem. and Met. Eng.*, 1919, **27**, 11.

[3] Rössing, *Z. anal. Chem.*, 1902, **41**, 9; *J. Chem. Soc. Abstr.*, 1902, **82**, 230.

[4] *Inaug. Dissertation*, Zurich, 1909; *J. Inst. Metals*, 1910, **4**, 319.

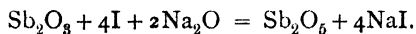
[5] Cf. *Quantitative Analysis by Electrolysis*, A. Classen, 1919; also, *Electro-Analysis*, E. F. Smith, 1908, p. 171.

the deposition (in a sand-blasted dish) is hastened, so that 0·3 to 0·4 g. of antimony is completely separated in from one and a half to two hours. If the deposition is carried out in the warm solution, the dish must be washed a few times with hot water (without breaking the current) and finally once with alcohol, then dried at 90°, either in an air bath or on a boiling water bath, and weighed when cold. The antimony, which is especially adherent to the inside of the matted dish (p. 229), is dissolved off by a mixture of nitric and tartaric acids. In the usual course of the analysis of ores, etc., by fusion with sodium carbonate and sulphur, or by treatment of the sulphuretted hydrogen precipitate with sodium or potassium sulphides, antimony solutions are obtained which may be directly electrolysed after first decomposing the polysulphides by the careful addition of hydrogen peroxide, and then adding a considerable quantity of a cold, saturated solution of pure sodium sulphide. Arsenic is previously removed from the sulphuretted hydrogen precipitate by extraction with a saturated solution of ammonium carbonate, while tin may be present and is not deposited from a concentrated solution of the sulpho-salts.[1] After the deposition of the antimony, the tin may be precipitated as sulphide from the diluted solution by acidifying with sulphuric acid, and then converted into stannic oxide and weighed as such.

N. K. Clancy[2] uses ammonium polysulphide as an electrolyte and electrolyses with rotating anode at the boiling point, the initial voltage being 3·5 and the current density 1 ampere per square decimetre. Any tin present is deposited with the antimony, and under these conditions the deposited metal is quite bright. A. Lassieur[3] recommends the use of a platinum gauze cathode coated electrolytically with mercury. This gives a clean grey deposit which may be dried at 100°.

II. Volumetric Methods

1. Titration with Iodine (F. Mohr).—The oxidation takes place in a slightly alkaline solution, according to the equation :—

$$Sb_2O_3 + 4I + 2Na_2O = Sb_2O_5 + 4NaI.$$

According to Fresenius, a solution containing about 0·1 g. of antimony oxide, prepared by addition of water and tartaric acid, is neutralised with sodium carbonate, 20 c.c. of a cold, saturated solution of sodium bicarbonate and some starch solution added, and then titrated to the blue coloration with a standard iodine solution. Finkener adds a slight excess of the iodine solution, and titrates back, till the blue coloration just disappears, with a solution of sodium thiosulphate

[1] *Cf.* A. Fisher, *Z. anorg. Chem.*, 1904, **42**, 363 ; *J. Soc. Chem. Ind.*, 1905, **24**, 153.
[2] *J. Amer. Chem. Soc.*, 1913, **35**, 1482. [3] *Compt. rend.*, 1923, **177**, 263.

checked against the iodine solution. One g. I = 0·5743 g. Sb_2O_3, or = 0·4798 g. Sb.[1]

2. **Titration of the Iodine liberated by the action of Antimonic Chloride on Potassium Iodide in Hydrochloric Acid Solution** (Parry[2]).—This method is suitable for alloys of lead, tin, and antimony. Copper, arsenic, and iron, if present, are included with the antimony in the determination, and must be separately determined and allowed for. One to two grams of the finely divided alloy is dissolved in hydrochloric acid, potassium chlorate solution being added towards the end to assist solution. An excess of potassium chlorate is then added, the solution diluted, and the chlorine boiled off; after allowing to cool, the flask is filled with carbon dioxide from a Kipp apparatus, 20 c.c. of a 20 per cent. potassium iodide solution added, and the solution titrated rapidly with stannous chloride.

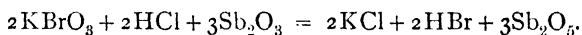
The allowance for arsenic, copper, and iron is as follows:—

1 per cent.	As	=	1.6	per cent. Sb.
1 ,,	Cu	=	0.945	,,
1 ,,	Fe	=	1.07	,,

Giraud[3] adds carbon bisulphide to take up the liberated iodine, and titrates with sodium thiosulphate.

3. **Titration with Potassium Bromate.**—This method was originally proposed by S. Györy[4] and has been modified by H. Nissenson and P. Siedler[5] and by R. W. Rowell.[6]

The potassium bromate solution is made up by dissolving 2·7852 g. of recrystallised potassium bromate dried at 100° and diluting the solution to 1 litre; 1 c.c. corresponds exactly to 6 mg. of antimony according to the equation:—

$$2KBrO_3 + 2HCl + 3Sb_2O_3 = 2KCl + 2HBr + 3Sb_2O_5.$$

During the titration methyl orange (two drops of a solution of 0·5 g. of solid methyl orange in 500 c.c. water) is used as an indicator, and when the red colour disappears the titration is finished (*cf.* Hard Lead, p. 238).

4. **Titration with Potassium Permanganate.**—This method is particularly suitable for alloys containing antimony and free from iron and arsenic, which interfere.

One g. of the alloy is dissolved in 25 c.c. of concentrated sulphuric acid in a 250 c.c. round-bottomed flask, heating gently at first, and

[1] *Cf.* E. G. Beckett, *J. Inst. Metals*, 1910, **4**, 320; J. Knop, *Z. anal. Chem.*, 1923, **63**, 81; O. Collenberg and G. Bakke, *Z. anal. Chem.*, 1923, **63**, 229.

[2] *Assay of Tin and Antimony*, p. 39.

[3] *Bull. Soc. Chim.*, 1887, **46**, 504; *J. Chem. Soc. Abstr.*, 1887, **52**, 400.

[4] *Z. anal. Chem.*, 1893, **32**, 415; *J. Chem. Soc. Abstr.*, 1893, **64**, 554.

[5] *Chem. Zeit.*, 1903, **27**, 749; *J. Soc. Chem. Ind.*, 1903, **22**, 967.

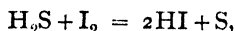
[6] *J. Soc. Chem. Ind.*, 1906, **25**, 1181.

eventually boiling until solution is complete and no black residue remains. The solution is allowed to cool, 30 c.c. of water and 5 c.c. dilute hydrochloric acid (1 : 4) added, after which the solution is boiled to expel sulphur dioxide and again cooled. After bringing the volume of solution to not less than 100 c.c. it is titrated with standard potassium permanganate until a permanent pink tint is obtained. The standard solution should contain 3·21 g. of potassium permanganate per litre, and may be standardised against pure metallic antimony. The value of the solution in antimony is equal to its value in iron multiplied by 1·0714.[1]

L. Bertiaux[2] recommends the addition of 10 g. anhydrous sodium or potassium sulphate to the sulphuric acid used for the solution of the alloy and also the addition of two drops of 1 : 1000 solution of Poirrier orange (or indigo) to the solution before titration; the slightest excess of permanganate liberates chlorine which decolorises the solution.

The following modification due to M. F. Coolbaugh and J. O. Betterton[3] is used for ores, etc. The ore or other material is decomposed by means of ammonium persulphate, thus avoiding losses by volatilisation during fusion. The weighed portion together with eight to ten times its own weight of ammonium persulphate is placed in an Erlenmeyer flask and the mass fused at a low temperature, the temperature being gradually raised. After cooling, the mass is dissolved in hydrochloric acid and diluted to 100 c.c. Sulphuretted hydrogen is passed for fifteen minutes, the precipitate filtered off, dissolved in strong hydrochloric acid, with the aid of a little potassium chlorate. The solution is diluted, two drops of ferric chloride added, the temperature kept at 90°, and then stannous chloride added until the yellow colour of the ferric chloride just disappears. The whole solution is now poured into a beaker containing 10 c.c. saturated mercuric chloride solution, diluted to 500 c.c. and titrated with potassium permanganate.

5. Titration of the Sulphuretted Hydrogen evolved from Antimony Sulphide (R. Schneider[4]).—Antimony tri- and pentasulphide liberate sulphuretted hydrogen on boiling with hydrochloric acid; at the same time sulphur separates from the pentasulphide. If the evolved sulphuretted hydrogen is led into a measured excess of iodine solution, considerably diluted with water, contained in a large retort, sulphur separates according to the equation:—

$$H_2S + I_2 = 2HI + S,$$

and the excess of iodine can be titrated back with a sodium thiosulphate solution checked against the iodine solution. The starch solution is not added in this case until the solution is of a wine-yellow colour.

[1] *Cf.* O. Collenberg and O. Bakke, *Z. anal. Chem.*, 1923, **63**, 229.
[2] *Chimie et Industrie*, 1920, **4**, 467; *J. Inst. Metals*, 1921, **25**, 434.
[3] *Western Chemist and Metallurgist*, vol. iv., p. 229.
[4] *Pogg. Ann.*, 1860, **110**, 634.

Sb_2S_3 evolves $3H_2S$, which requires 6I for oxidation. One gram of iodine used, therefore, corresponds to 0·3198 g. Sb.

The determination is carried out as follows:—The filter paper containing the antimony sulphide (which may be admixed with arsenic sulphide) is introduced into a wide-necked flask, and 25 per cent. hydrochloric acid allowed to run in through a safety funnel. The long delivery tube is inserted into the body of the retort, which is inverted, filled with dilute iodine solution, and rests on a wicker stand. The flask is heated and the liquid allowed to boil for ten minutes; the delivery tube is withdrawn from the iodine solution during the boiling. The retort is then cooled under the tap, the iodine solution washed into a large beaker, and the excess of iodine titrated back. As a check, the antimony solution in the flask may be titrated by Mohr's method (p. 285), after the addition of tartaric acid, diluting, and filtering. Since the antimony sulphide precipitate generally contains chlorine, this method does not give absolutely accurate results, but may be employed for technical determinations.

III. Separation of Antimony, Arsenic, and Tin

The best methods of separation have already been described under the analysis of Hard Lead, p. 237, and of White-metal, p. 265. Arsenic and antimony are separated by diluting the solution of the sulphides in hydrochloric acid and potassium chlorate after the addition of tartaric acid, filtering, saturating with ammonia, and precipitating the arsenic acid with magnesia mixture, etc. A small quantity of arsenic may be extracted from the mixed sulphides by means of a saturated solution of ammonium carbonate. Tin and antimony are best separated by means of iron, the metallic antimony being redissolved and determined, and the tin in solution precipitated as sulphide from the antimony-free solution or titrated with iodine. If arsenic and tin are present together with antimony, it is best to precipitate the arsenic as pentasulphide by passing sulphuretted hydrogen into the cold, strong hydrochloric acid solution, to filter through an asbestos filter, oxidise the filtrate with a slight excess of bromine water, dilute somewhat, and precipitate the antimony by means of pure iron, etc.

Hampe[1] uses the following method of separation:—After adding a fair quantity of tartaric acid to the solution and precipitating the arsenic as magnesium ammonium arsenate, the filtrate is acidified, sulphuretted hydrogen passed in, the tin and antimony sulphides dissolved in freshly prepared sodium sulphide solution, and the concentrated, cold solution of the sulpho-salts oxidised by the addition of small quantities of sodium peroxide until a fresh addition causes

[1] *Chem. Zeit.*, 1894, **18**, 1900; *J. Soc. Chem. Ind.*, 1895, **14**, 302.

effervescence with evolution of oxygen. To bring about complete separation of the sodium pyroantimoniate, after boiling and cooling, one-third of the volume of alcohol of sp. gr. 0·833 is added, and the precipitate filtered off after standing for twenty-four hours. Rose recommends washing the precipitate first with a mixture of equal volumes of water and alcohol (sp. gr. 0·83), and then with a mixture of one volume of water and three volumes of alcohol; a few drops of sodium carbonate solution should be added to the liquids used in the washing. The sodium pyroantimoniate is dissolved in hydrochloric acid containing tartaric acid, and the antimony precipitated by sulphuretted hydrogen and finally weighed as oxide. The alcohol is driven off from the filtrate from the sodium pyroantimoniate, the solution acidified with hydrochloric acid, sulphuretted hydrogen passed in, and the precipitate of tin sulphide converted by careful ignition into oxide, which is finally strongly ignited after the addition of a small piece of ammonium carbonate.

L. Hahn and P. Phillipi[1] add to the solution containing the thio-salts of the metals, sodium hydroxide or hydrogen peroxide, which causes the precipitation of sodium pyroantimoniate. Tin is then precipitated as stannic oxide from the filtrate by means of ammonium nitrate, and arsenic from the final filtrate as magnesium ammonium arsenate; the last precipitate should be purified by reprecipitation.

IV. Special Methods

1. For Ores, Liquated Stibnite, and Slags.

(*a*) One-half to one gram of the finely ground substance is fused in a covered porcelain crucible with six times its weight of a mixture of equal parts of sodium carbonate and sulphur (or six times the weight of sodium thiosulphate dehydrated at 210°) until no more sulphur is evolved. The cold melt is extracted with 40 to 50 c.c. of hot water, the solution filtered into a matted Classen dish, concentrated by evaporation on the water-bath, the polysulphides decomposed by the careful addition of hydrogen or sodium peroxide, the volume of the solution made up to 150 c.c. after the addition of 60 to 70 c.c. of a cold, saturated solution of sodium sulphide, and then electrolysed hot (*cf.* Method **2**, p. 284). If the substance contains arsenic in considerable quantity, the sulpho-salts in the aqueous extract of the fusion are completely oxidised by repeated additions of small quantities of sodium peroxide (arsenic is thereby converted into sodium arsenate), the solution digested with a large quantity of cold, saturated sodium sulphide solution until all the sodium pyroantimoniate is completely dissolved, and then electrolysed;

[1] *Z. anorg. Chem.*, 1921, **116**, 21; *J. Inst. Metals*, 1922, **27**, 436.

by this means arsenic acid is not reduced. The antimony is removed from the dish by alternately warming with strong nitric acid and hot potassium hydroxide, or with nitric and tartaric acids.

If electrolytic apparatus is not available, the solution of the sulpho-salts from the fusion is warmed with excess of dilute sulphuric acid, the sulphides filtered off, the antimony separated if necessary from arsenic and tin, and determined finally as oxide (Method 1, p. 284).

Oxide ores, difficultly soluble in acids, are likewise treated by fusion with sodium carbonate and sulphur, etc. (*Cf.* also Estimation of Antimony in Arsenic Ores, p. 280.)

(*b*) The finely ground ore or liquated stibnite is dissolved in aqua regia, or in hydrochloric acid and potassium chlorate, the solution made alkaline with potassium hydroxide, sodium sulphide solution added, warmed until all sodium pyroantimoniate has dissolved, filtered, and after adding a large quantity of sodium sulphide solution, the solution is electrolysed with a current of 2 ampères. Arsenic is not deposited, since it is present as arsenic acid. The usual analytical method may of course also be applied to this solution.

(*c*) The volumetric method of titration with potassium bromate is applicable to sulphide and oxide ores. Of the former 0·3 g. of finely ground ore is weighed out, dissolved by heating with 20 c.c. hydrochloric acid and 5 c.c. of a saturated solution of bromine in hydrochloric acid, and, when completely dissolved the solution is reduced and titrated as described for alloys.

Oxide ores require to be fused with sodium peroxide (1 of ore to 10 of peroxide), after which the melt is dissolved in water, acidified with hydrochloric acid, 10 c.c. of acid added in excess and the volume made up to 150 c.c. After adding 1 g. tartaric acid, warming and passing sulphuretted hydrogen, the precipitated antimony sulphide is filtered off, washed, dissolved in hydrochloric acid-bromine solution and treated as already described.

(*d*) *Determination of Sulphur.*—Several decigrams of the ore is heated in a current of chlorine, tartaric and hydrochloric acids added to the liquid in the receiver, the free chlorine expelled from the solution by warming and passing in carbon dioxide, antimony, arsenic, and tin precipitated by sulphuretted hydrogen (Finkener), the sulphides filtered off, the sulphuretted hydrogen in the filtrate boiled off, and the sulphuric acid precipitated as usual with barium chloride solution.

2. **For Metallic Antimony** (Regulus Antimonii).

Commercial antimony generally contains lead, silver, arsenic, copper, iron, and a little sulphur as impurities ; bismuth, nickel, and cobalt may be present. The pure metal has a silver-white colour, while antimony containing lead is more or less of a bluish white colour with a fracture

less coarsely crystalline than that of the pure metal. In commerce, the so-called antimony star[1] on the top of the ingot or cake is taken as a special sign of purity; this is only formed on the pure metal, however, if it solidifies under a covering of slag and is protected against shock.

For the analysis, several grams of the finely pulverised metal are dissolved in nitric and tartaric acids, the solution saturated with ammonia, copper, lead, and iron precipitated by the careful addition of sulphuretted hydrogen (Finkener's method, p. 264), the sulphides filtered off, and the metals determined in the usual way. For the determination of the arsenic a separate sample of several grams is dissolved in hydrochloric acid and potassium chlorate, the chlorine driven off by gently warming, the solution cooled, made up to contain two-thirds of its volume of concentrated hydrochloric acid, sulphuretted hydrogen passed in for a long time, arsenic and copper precipitated as sulphides and filtered off through an asbestos filter (*cf.* Analysis of White-metal, p. 268). The arsenic sulphide is extracted with ammonium carbonate solution, the solution evaporated, oxidised with strong nitric acid, and the arsenic acid precipitated in the usual way with magnesia mixture, leaving the copper in the ammoniacal solution.[2]

The method described on p. 266 gives good results provided that during the distillation a temperature of 119° is reached but not exceeded.

The determination of sulphur is carried out as described under (*d*) (p. 290).

3. For Antimony Alloys.

The methods of analysis have already been described under the analysis of Hard Lead (p. 236), and of White-metal (p. 265).

4. For Antimonial Preparations and Colours.

(Oxides, Tartar Emetic, Gold Sulphur, Antimony Cinnabar, etc.)

These are either dissolved or fused with sodium carbonate and sulphur, and their content of antimony determined by the methods on pp. 284-8. For antimony pigments see pp. 464 *et seq.* For antimony salts see p. 394.

[1] A specimen of antimony from Hungary possessing this star-like surface contained the following impurities:—Arsenic, 0·330 per cent.; iron, 0·052 per cent.; and sulphur, 0·720 per cent. (Schnabel).

[2] *Cf.* Groschuff, *Z. anorg. Chem.*, 1918, 103, 164.

ZINC

The products that require technical examination are:—Raw and calcined ores and waste from the dressing of the ores, commercial zinc, zinc dust, hard zinc or bottom zinc from the galvanising of iron, zinc dross and ashes, materials from the metallurgical treatment of lead, copper, and iron ores containing zinc, zinc white residues, and fumes. In addition, especially in zinc works proper, crude or work zinc has to be analysed as well as the residues from the distillation of zinc.

The most important ores of zinc are:—

Zinc blende or *Blende*, ZnS, contains in its purest state 67 per cent. of zinc, but invariably contains iron as impurity, and cadmium from traces up to 3 per cent. Many black blendes contain manganese and traces of tin, less frequently traces of indium and gallium also. Pyrites, galena, copper pyrites, arsenic, and antimony ores are frequently found with blende.

Calamine or *Smithsonite*, $ZnCO_3$, containing 52 per cent. of zinc; a part of the zinc in the carbonate is usually replaced by iron, manganese, cadmium, calcium, and magnesium. The green calamine of Laurion is coloured with copper carbonate; rich deposits of calamine have also been found there in antique aqueducts. Common calamine, with less than 30 per cent. of zinc and mixed with clay, ferric hydroxide, manganese oxide, limestone, and dolomite, is much more frequent.

Hemimorphite, $Zn_2SiO_4+H_2O$, contains 53·7 per cent. of zinc, and is known as "electric calamine" when associated with the frequently occurring earths, clays, etc., as impurities.

Willemite, Zn_2SiO_4, containing 58·1 per cent. of zinc, and *Troostite*, $2(Zn,Mn)O,SiO_2$, as well as *Zincite* or *Red Zinc Ore* (zinc oxide with up to 12 per cent. of manganese as oxide) and *Franklinite*, $3(FeZnMn)O+(FeMn)_2O_3$, are found in large quantities exclusively in the state of New Jersey.

Methods of Determination

In technical work the zinc in ores, etc. (with the exception of alloys of zinc with copper, nickel, etc.), is preferably determined, volumetrically, either by the titration of the ammoniacal solution with sodium sulphide (Schaffner's method), or by the potassium ferrocyanide method; the latter method is generally employed in England and in the United States, the former method in Germany. The gravimetric determination of the zinc as zinc sulphide is rarely used in commercial work. Up to the present, none of the many electrolytic methods proposed has found application to the determination of zinc in ores.

I. Gravimetric Methods

1. **Determination of the Zinc as Sulphide,** ZnS.—This method permits of a simple and complete separation of zinc from the metals (iron, manganese, nickel, cobalt) which are not precipitated from a dilute mineral acid solution by sulphuretted hydrogen, and is best carried out in a very dilute solution rendered just acid with sulphuric acid. One-half to one gram of the dried finely ground substance (raw or calcined ore, residues, ashes, etc.) is dissolved in a flask in hot aqua regia (prepared from concentrated acids), or by heating with nitric acid saturated with potassium chlorate. Excess of previously diluted sulphuric acid is added, and the contents of the flask boiled until dense fumes of sulphuric acid are evolved. The syrupy residue is taken up with water (50 c.c.), sulphuretted hydrogen passed in, the precipitate (copper sulphide, cadmium sulphide, lead sulphate, gangue, etc.) filtered off, and washed with diluted sulphuretted hydrogen water acidified with sulphuric acid. The filtrate is boiled to expel the sulphuretted hydrogen, cooled, and after the addition of a piece of Congo red paper, neutralised with ammonia until the paper just turns a pale violet colour. Any cloudiness due to ferric hydroxide, etc., is removed by the addition of a few drops of normal sulphuric acid ; if the liquid becomes strongly heated (on account of its being strongly acid), after nearly neutralising, it is cooled by placing it in cold water, and then the cooled solution further neutralised. Litmus paper cannot be used, since neutral solutions of zinc sulphate and of zinc chloride are acid to litmus. The solution is diluted according to the amount of zinc it contains, so that 100 c.c. does not contain more than 0·1 g. of zinc. The beaker is then covered with a clock-glass and a continuous current of sulphuretted hydrogen[1] passed in for one and a half to two hours through a bent delivery tube with a fine opening. If the precipitation of the white zinc sulphide does not begin for a quarter of an hour or more, the solution contains too much free acid ; this will be recognised later by considerable amounts of zinc sulphide adhering fairly fast to the sides of the beaker. After standing twelve to eighteen hours, the solution is filtered through a strong, ash-free paper, the zinc sulphide brought on to the paper and washed with water (200 to 300 c.c.) in which about 5 g. of ammonium sulphate is dissolved, after the addition of some sulphuretted hydrogen water. A slight opalescent cloudiness of the filtrate, which generally does not appear till after the filtration, is due to very finely divided sulphur, which is formed by the action of the oxygen in the air on the sulphuretted hydrogen. Before bringing the precipitate on to the filter paper, another beaker is

[1] The conditions for quantitative precipitation of zinc sulphide have been studied by H. A. Falls and G. M. Ware, *J. Amer. Chem. Soc.*, 1919, 41, 487.

placed under the long-necked filter funnel, and the first runnings of the cloudy filtrate poured back until the pores of the filter paper become stopped up and the filtrate runs through perfectly clear. The filter paper with the precipitate is then dried in an air-bath, the zinc sulphide removed as completely as possible on to glazed paper, the paper ignited in a Rose crucible, previously weighed with the lid (the ignition requires about one hour), the zinc sulphide, together with an equal volume of powdered roll sulphur, introduced into the cooled crucible, the lid placed on, and pure dry hydrogen led in by means of the porcelain delivery tube. After all the air is driven out, the crucible is heated with a Bunsen burner with a small flame; when all the sulphur has escaped, the temperature is increased to a bright red heat, and after strongly igniting for twenty minutes, the crucible is allowed to cool in the current of hydrogen. The zinc sulphide precipitate may alternatively be filtered on a carefully prepared asbestos filter in a Gooch crucible. $ZnS \times 0{\cdot}6710 = Zn$.

The filtrate from the zinc sulphide is evaporated in a large porcelain dish over a free flame to about 200 c.c., after cooling, neutralised with ammonia, using Congo red paper as indicator, very slightly acidified with a little normal sulphuric acid, and then sulphuretted hydrogen passed in for an hour. If any zinc sulphide separates after standing for some time, it is filtered off and treated as above. The precipitation in a very dilute hydrochloric acid solution is not to be recommended, because on ignition in hydrogen a loss of zinc as zinc chloride may take place owing to a small amount of ammonium chloride being retained in the dry zinc sulphide. A yellow deposit on the under side of the crucible lid is cadmium sulphide; this is sometimes found in determining zinc in brass or German silver, when the copper is determined electrolytically, and the solution from the copper neutralised, diluted, and the zinc precipitated with sulphuretted hydrogen. The deposit is weighed together with the zinc sulphide as such, since the separation or quantitative determination of the very small quantity of cadmium is superfluous.

In the analysis of German silver (*cf.* Nickel, p. 334) several cubic centimetres of distilled sulphuric acid are added to the filtrate from the zinc sulphide before evaporation, otherwise nickel sulphide easily separates and adheres firmly to the sides of the dish. On subsequent neutralisation of the solution with ammonia, a corresponding quantity of ammonium sulphate is formed, the presence of which is an advantage in the electrolytic deposition of the nickel.

2. The Electrolytic Determination of Zinc is of but little practical importance, since good adhesive deposits of the metal are obtained only by very slow deposition, and it is essential to work with nearly pure zinc solutions. According to Classen, good results are obtained,

for example, if a sulphuric acid solution containing several decigrams of zinc is neutralised with potassium hydroxide, 4 to 5 g. of neutral potassium oxalate added, warmed to dissolve any precipitated zinc oxalate, 4 to 5 g. of potassium sulphate dissolved in the solution (about 100 c.c.), which is then cooled and electrolysed, first with a current of 0·25 to 0·5 ampère, and finally with 1 ampère. The zinc is not deposited directly on to the platinum electrode (cone or dish), but this latter is first coated with a clean electrolytic deposit of copper or silver, since zinc deposited directly on to platinum alloys with it, and when dissolved off the electrode by means of acids leaves behind peculiar dark spots, and the weight of the electrode after repeated ignition and treatment with hydrochloric acid does not keep constant. For coating the dish with copper, a copper sulphate solution acidified with nitric acid or a potassium copper cyanide solution is used; and for silvering, the usual silvering solution of potassium silver cyanide, containing 4 to 10 g. of silver and 10 to 25 g. of potassium cyanide per litre; it is, however, more practical to use dishes of fine silver. The use of copper gauze, plated with silver, is recommended by O. L. Barnebey.[1] When using a silvered or coppered cone or dish, the end of the deposition is determined either by adding about 20 c.c. of a cold, saturated potassium sulphate solution and electrolysing for another hour, or by taking out a few cubic centimetres by means of a pipette and warming with ammonium sulphide. The washing is done without breaking the circuit, and the cone dipped into water, then into absolute alcohol, and dried quickly over a heated dish. Small quantities of iron are deposited as metal along with the zinc; the zinc containing iron is dissolved off the silvered or silver electrode in warm dilute sulphuric acid, the solution cooled, the iron titrated with potassium permanganate and deducted.

E. F. Smith[2] states that zinc is readily determined by means of a rotating anode and mercury cathode; he uses a zinc sulphate solution containing free sulphuric acid.

The numerous other methods proposed for the electrolytic estimation of zinc are described in the literature on electrolytic analysis.[3]

II. Volumetric Methods[4]

1. Schaffner's Method (*cf.* Vol. I., p. 383).—This consists in the precipitation of the zinc in an ammoniacal solution as zinc sulphide by means of a sodium sulphide solution, which is added until a slight excess is recognised by means of an indicator. Iron, copper,

[1] *J. Amer. Chem. Soc.*, 1914, **36**, 1144.

[2] *Electro-Analysis*, p. 120.

[3] *Cf.* p. 170; also Baxter and Grose, *J. Amer. Chem. Soc.*, 1916, **38**, 868; Zublena, *Annali. Chim. Appl.* 1914, **1**, 302.

[4] *Cf.* "Technical Assay of Zinc," Greenwood and Brislee, *J. Inst. Metals*, 1909, **2**, 249.

lead, cadmium, manganese, nickel, and cobalt interfere with the accuracy of the method, and must previously be removed; the two latter hardly ever occur in appreciable quantities in ores of zinc. Sulphide ores (raw and calcined blendes) and residues are dissolved in strong nitric acid, aqua regia, brom-hydrochloric acid, or in nitric acid and potassium chlorate, calamine in aqua regia; electric calamine is best dissolved in 50 per cent. sulphuric acid with addition of hydrofluoric acid (in a platinum dish), evaporated, and the iron oxidised with a little nitric acid. The metals precipitated by sulphuretted hydrogen (lead, copper, and cadmium) are removed by passing the gas into the moderately dilute solution; the filtrate is boiled, the ferrous salts oxidised by the addition of nitric acid or aqua regia, the solution much diluted, bromine water added, then saturated with ammonia and ammonium carbonate solution, and the iron and manganese precipitate filtered off. If the ore contains above 5 per cent. of iron, it is redissolved in dilute sulphuric acid, after washing the precipitate for a short time, bromine water (10 to 20 c.c.) added to the diluted solution, and the precipitation repeated, since the ferric hydroxide precipitate carries down with it a considerable quantity of zinc hydroxide.

The precipitation may also be effected in a 500 c.c. graduated flask, which is filled to the mark after cooling, shaken round, and not taking into account the volume of the precipitated ferric hydroxide, several hundred cubic centimetres are filtered through a dry filter paper, and 100 c.c. taken for each titration; in this case it is well to prepare the solution of chemically pure zinc which is to be used as standard in a similar graduated flask, and to add approximately the same amount of iron (as ferric chloride solution), to dilute, add excess of ammonia and ammonium carbonate, make up to 500 c.c., etc. The amount of zinc retained by the ferric hydroxide precipitate is then approximately the same in both solutions. This method is quicker than the above.

The excess of ammonia in the solutions to be titrated must be slight; it is usual to allow solutions withdrawn by the pipette to stand uncovered overnight. The sodium sulphide solution is prepared from a cold, saturated solution of pure crystallised sodium sulphide by diluting with ten to twenty times the volume of distilled water and connecting up a large stock bottle permanently with a burette. The best indicator for the end-point is "Polka paper," a paper sized and covered with white lead; it is prepared for the use of laboratories. The titration is carried out in beakers and the solution stirred with a glass rod, which serves for the removal of drops of liquid from time to time which are allowed to drop on to the test paper. A modification of the method of titration consists in adding to the solution, contained in a flask, flakes of freshly precipitated ferric hydroxide, keeping the

solution rapidly rotating during the addition of the sodium sulphide solution and continuing until the flakes are blackened. The flakes are prepared by allowing one drop of ferric chloride solution to fall into a little ammonium hydroxide (0·880) contained in a watch glass and pouring off the excess liquid. Direct contact of the sulphide solution with the indicator must be avoided, otherwise darkening occurs before the end-point is reached. The flask is sometimes held over a plate-glass mirror to facilitate the observation of the flakes. The method is sufficiently accurate for all technical purposes.

2. Galletti's Potassium Ferrocyanide Method.—This method, modified by Fahlberg,[1] v. Schulz, Low,[2] and others, consists in precipitating the zinc by means of a solution of potassium ferrocyanide in a solution warmed to 60° to 80°, acidified with hydrochloric acid, and free from iron, manganese, copper, lead, and cadmium, the end-point being recognised by a spot test, using a solution of uranium acetate as indicator.

According to V. Lenher and C. C. Meloche[3] the presence of lead is without influence on the titration in hydrochloric acid solution, as lead can only be titrated with ferrocyanide in acetic acid solution, a small quantity of mineral acid being sufficient to prevent precipitation.

This method is generally used in preference to the sodium sulphide method, both in England and in America, as the standard solution is more stable.

The method of solution for the ore and the separation of the interfering metals may be carried out as described under Schaffner's method. The alkaline solution thus obtained is neutralised with hydrochloric acid, an excess of 5 c.c. added, the solution made up to 250 c.c. with hot water, and titrated. The solution of potassium ferrocyanide contains 22 g. of the crystallised salt to the litre; a 5 per cent. solution of uranium acetate is used as indicator. Uranium nitrate or ammonium molybdate may also be used as indicators.[4]

The titration in an ammoniacal tartrate solution (see Special Methods, Voigt, p. 298) is sometimes used.

III. Special Methods of Analysis

1. For Ores, Calcined Ores, Ashes, Residues, etc.

Loss on Ignition.—A few grams of calamine or electric calamine are weighed in a porcelain crucible, gradually heated up to strong ignition, and the loss in weight (carbon dioxide and water) determined after cooling.

[1] Fresenius, *Quantitative Analysis*, 7th ed., vol. ii., p. 283.
[2] *Berg. u. Hütten. Zeit.*, 1893, **52**, 338.
[3] *J. Amer. Chem. Soc.*, 1913, **35**, 134. *Cf.* E. Nyman, *Chem. News*, 1919, **119**, 75.
[4] Nissenson and Kettembeil, *Chem. Zeit.*, 1905, **27**, 591.

Sulphur (*cf.* Vol. I., p. 383).

In the working of the calciners, the roasted blendes are tested to see if sufficiently calcined by gently warming a measured quantity of the fine powder in a small flask with 10 c.c. of hydrochloric acid (1 : 2), at the same time holding a strip of filter paper moistened with a dilute alkaline solution of lead acetate in the neck of the flask. The degree of calcination is judged from the intensity of the coloration produced on the paper.

Zinc—Voigt's Volumetric Method.—Forty-six grams of pure crystallised potassium ferrocyanide is dissolved and the solution made up to 1 litre. For standardising, 12·45 g. of chemically pure zinc oxide is dissolved in hydrochloric acid, the solution diluted up to 1 litre, and stored in a well-stoppered bottle. One c.c. contains exactly 10 mg. of zinc. Ten c.c. is withdrawn with a pipette, 10 c.c. of a solution of tartaric acid (200 g. in 1 litre), 10 c.c. of a ferric chloride solution (60 g. in 1 litre), and 100 c.c. of water added, ammonia added in slight excess, and the solution titrated with the solution of potassium ferrocyanide, until a permanent blue colour is produced on removing a drop and adding it to acetic acid (1 : 3) on a pitted porcelain plate. The first definite blue coloration must be taken as the finishing point; this should show immediately and is not to be confused with the blue colour which appears after standing one or two minutes. After carrying out the preliminary and control titrations, the solution of potassium ferrocyanide is diluted so that 1 c.c. corresponds accurately to 10 mg. of zinc.

For the determination, 1 g. of the finely ground ore, dried at 100°, is warmed with 10 c.c. of fuming hydrochloric acid until all the sulphuretted hydrogen is completely driven off, 3 c.c. of fuming nitric acid is then added, and the solution considerably evaporated, but not quite to dryness. Ten c.c. of the solution of tartaric acid is then added, also 10 c.c. of the ferric chloride solution, if necessary, the solution made slightly ammoniacal, diluted with water to 100 to 120 c.c., and titrated as above.

Lead and Iron.—Five grams of the finely ground and sieved ore is dissolved in hydrochloric acid and fuming nitric acid, 10 c.c. of distilled sulphuric acid added, and the solution boiled till white sulphuric acid fumes are evolved. The cooled mass is moistened with 75 c.c. of water, and then boiled and cooled. The separated lead sulphate, together with the gangue, is filtered off, washed, and the filter paper with its contents digested in a beaker with a concentrated solution of sodium acetate or neutral ammonium acetate to dissolve the lead sulphate. The lead in this solution may be determined volumetrically by titration with ammonium molybdate solution using tannin as an indicator (see p. 230), or may be determined

gravimetrically as follows:—The solution is filtered through a smooth filter paper which is well washed with water containing acetate, the lead in the filtrate precipitated with potassium bichromate, and after settling, the precipitate filtered off on to a Gooch crucible and washed ten times with warm water. The crucible is then removed from the filter-flask, cleaned externally and dried, first in an air bath, and finally at about 200°. $PbCrO_4 \times 0{\cdot}6411 = Pb$.

The iron is determined in a twentieth part of the filtrate from the lead sulphate and gangue, by reducing with zinc after the addition of sulphuric acid, testing with potassium thiocyanate, and titrating the cooled solution, acidified with sulphuric acid, with potassium permanganate.

Fluorine[1].—It is frequently necessary to determine fluorine in zinc ores and concentrates, and the following is the standard method generally used.

Half to one g. of the material (according to the amount of fluorine present) is fused in a porcelain crucible with ten times its weight of a mixture of equal parts of sodium carbonate and potassium carbonate until the whole mass is in quiet fusion. The temperature is raised to bright redness, and the fused mass is poured into an iron mould. The crucible is broken into small pieces and transferred along with the fused mass to a 6-inch agate ware casserole (agate ware is preferable to porcelain as diminishing the liability to subsequent "bumping"). Two hundred c.c. of distilled water is added, and the whole digested for one hour at a temperature near the boiling point, the fused lump being broken up with a thick glass rod. If, at the end of this time, any undecomposed lumps are noticed, they are removed with the pincers and ground in an agate mortar and washed back into the casserole with hot water.

The whole is boiled for ten minutes and filtered through a loose filter into a beaker of about 1 litre capacity and washed first with hot water then with a hot solution of ammonium carbonate. The residue is discarded. To the filtrate 10 g. of ammonium carbonate is added and the solution boiled for five minutes, and afterwards allowed to stand in the cold for two hours. It is then filtered through a loose filter into a 6-inch agate ware casserole (as much as possible of the fluid being decanted) and washed with cold water once or twice. In order to eliminate traces of silica, 20 c.c. of an emulsion of zinc oxide in ammonia is added and boiled with the casserole uncovered, until the odour of ammonia is no longer detected. It is then filtered into a beaker and washed with hot water. To the filtrate a solution of calcium chloride is added while stirring with a rubber-tipped glass rod, until no more precipitate is formed. The precipitate is allowed to subside, filtered

[1] *Cf.* also Vol. I., p. 387.

and washed with hot water. The filtrate is tested for carbonates and fluorine with a few drops of the calcium chloride solution. The precipitate is transferred along with the filter paper to a platinum dish of suitable size, dried and then ignited at a red heat for twenty minutes. It is cooled and the mass disintegrated with hot water. Acetic acid is added until the solution is clear, which is then evaporated to dryness. The mass is moistened again with acetic acid and evaporated until the odour of acetic acid is no longer perceptible.

The mass is washed into a beaker with hot water, hot water added until the calcium acetate is dissolved, then about 150 c.c. more of hot water is added, and the solution well stirred, digested for a few minutes at a gentle heat and filtered, washed first with hot water and then with hot ammonium chloride solution, and again with hot water. The precipitate and filter paper are transferred to a platinum dish, dried and ignited. After cooling and moistening with cold water, 6 c.c. of strong sulphuric acid is added and heated for a few minutes, then cooled, diluted and transferred to a beaker. Five g. of ammonium chloride is added, the liquid boiled for a few minutes, cooled, and an excess of strong ammonia water added. Then 2 or 3 c.c. of strong hydrogen peroxide solution is added, boiled and filtered. The calcium is precipitated from the filtrate with ammonium oxalate and determined as CaO in the usual manner by titration with permanganate. $CaO \times 0{\cdot}6763$ = fluorine.

Coincidently with the above determination there should be carried out a "blank" experiment, employing the same reagents in the same quantities, and carried out in precisely the same manner as the above, but with the omission of the material under analysis. The result of this "blank," if any, is deducted from the result arrived at in the determination on the ore.

2. For Metallic Zinc (*Crude Zinc*, *Spelter*, *and Zinc Dust*).

(*a*) *Crude Zinc.*—This invariably contains lead, some iron, cadmium, suspended carbon, and traces of sulphur as impurities; in addition, small quantities of tin, copper, silver, and arsenic are frequently present, traces of antimony and silicon being rarely found.

In smelting works only the lead and iron are usually determined. Five grams of the cut-up borings from several plates are warmed in a covered porcelain dish with 50 c.c. of dilute sulphuric acid (1 : 4), and after the evolution of hydrogen has ceased 1 c.c. of nitric acid (sp. gr. 1·2) is added. The solution is evaporated and heated on the sand-bath until sulphuric acid fumes are copiously evolved, after which the cooled residue is heated for some time on a boiling water bath with 50 c.c. of water, the solution then cooled, the lead sulphate collected on a small filter paper, and determined in the usual way. To an aliquot part of

the filtrate (100 c.c.), 5 c.c. of ordinary 25 per cent. hydrochloric acid is added, and sulphuretted hydrogen passed in; the cadmium sulphide thus precipitated may be determined as described below. For the determination of the iron, 5 to 10 g. of the drillings are dissolved in hot, dilute sulphuric acid, the solution decanted off from undissolved lead, and the iron titrated in the cooled solution with potassium permanganate.

(*b*) *Commercial Zinc* (*Refined Zinc*).—This contains the same impurities as crude zinc in smaller quantities. The following method of F. Mylius and O. Fromm[1] gives very good results:—Two hundred c.c. of water is poured over 100 g. of an average sample in a flask of about 2 litres capacity, and the amount of nitric acid necessary for solution added in several portions, finally heating. The solution is then cooled, an excess of ammonia added until all the zinc hydroxide is redissolved, diluted to about 2 litres, and very dilute ammonium sulphide solution added in small quantities, shaking the solution round during the addition, until the freshly-formed precipitate appears white, like pure zinc sulphide. On warming the solution to 80°, the precipitated zinc sulphide is quickly decomposed by the other metallic salts, so that all the lead, cadmium, copper, silver, and bismuth pass into the precipitate. When the solution has cleared, it is filtered; the precipitate is then dissolved off the filter paper in hot dilute hydrochloric acid, whereby any copper and silver present as sulphides remain undissolved, and may be separated and determined in the usual way. The hydrochloric acid solution is evaporated with excess of sulphuric acid to separate the lead, the residue taken up with water, some alcohol added, and the lead sulphate filtered off. The alcohol in the filtrate is removed by evaporation, the solution neutralised with ammonia, 10 c.c. of 25 per cent. hydrochloric acid (sp. gr. 1·125) added for every 100 c.c. of liquid, and the cadmium precipitated as cadmium sulphide by passing in sulphuretted hydrogen for a long time. The precipitate is filtered off, dissolved in hot nitric acid (sp. gr. 1·2), the solution evaporated in a weighed porcelain crucible with a slight excess of sulphuric acid, the free sulphuric acid driven off, the residue gently ignited, and weighed as cadmium sulphate.[2] $CdSO_4 \times 0{\cdot}5392 = Cd$.

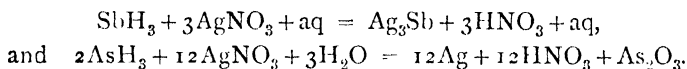
Barr's[3] method is somewhat similar but requires only 10 g. of the sample.

The sulphuretted hydrogen is expelled from the filtrate from the cadmium sulphide by boiling, the iron oxidised with bromine water, the solution saturated with ammonia, the ferric hydroxide filtered off, and dissolved in a little hydrochloric acid reprecipitated and finally weighed as ferric oxide.

[1] *Z. anal. Chem.*, 1897, **36**, 37.
[2] *Cf.* A. M. Fairlie, *Metal Ind.*, 1911, **3**, 16; *J. Inst. Metals*, 1911, **5**, 332.
[3] *J. Soc. Chem. Ind.*, 1924, **43**, 77.

Sulphur, arsenic, and antimony are determined by O. Günther's method.[1] One hundred grams of drillings obtained by boring completely through several plates, are placed in a large flask, the air in which is then completely driven out with a current of pure hydrogen, absolutely pure dilute sulphuric acid run in, and the evolved gas passed first through a wash-bottle containing potassium cadmium cyanide solution, and then through a second wash-bottle containing silver nitrate solution. When the evolution of hydrogen ceases, pure hydrogen is led into the flask for some time through the funnel tube which passes to the bottom of the flask and which is bent up at the end. In the first wash-bottle all the sulphur separates as cadmium sulphide, which is filtered off and converted into cadmium sulphate (see above) and weighed. In the second wash-bottle silver antimonide and metallic silver separate, whilst all the arsenic is in solution as silver arsenite. These decompositions take place in accordance with the equations:—

$$SbH_3 + 3AgNO_3 + aq = Ag_3Sb + 3HNO_3 + aq,$$

and $$2AsH_3 + 12AgNO_3 + 3H_2O = 12Ag + 12HNO_3 + As_2O_3.$$

The precipitate (silver and silver antimonide) is filtered off, dissolved in nitric and tartaric acids, the silver precipitated as chloride with hydrochloric acid, the antimony in the filtrate precipitated (after diluting and nearly neutralising) with sulphuretted hydrogen, and finally determined as antimony tetroxide. The arsenic present may be calculated from the above equations, if from the total silver given by the weight of silver chloride, the silver present as combined with antimony, is deducted; then $12\ Ag = 2As$.

When the zinc under examination is likely to contain a high percentage of lead (1 to 3 per cent.), it is advisable to separate the antimony, perhaps also the arsenic, by ordinary gravimetric methods, since under such conditions the antimony is not completely evolved as hydride on treatment with dilute sulphuric acid. The portion of the antimony in combination with the zinc, appears to be evolved as hydride, whilst the remainder is found to be associated with the residue of spongy lead.

If arsenic only is to be determined, 10 g. or more of the sample is oxidised by the addition, from time to time, of strong nitric acid, the solution evaporated, and the evaporation repeated with considerable quantities of pure hydrochloric acid. The solution is transferred to a flask, pure fuming hydrochloric acid and ferrous sulphate added, and all the arsenic distilled off as arsenic chloride (p. 205). Prauss' method (*cf.* Arsenic, Special Methods, **6**, p. 282) may also be employed and the sample dissolved in pure dilute sulphuric acid.

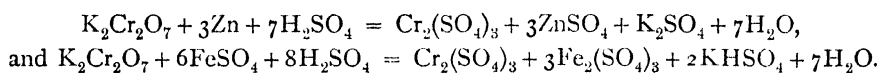
[1] *Z. anal. Chem.*, 1881, **20**, 503; *J. Soc. Chem. Ind.*, 1882, **1**, 118.

Tin is determined by digesting a large sample with an insufficient quantity of dilute sulphuric acid to effect complete solution, decomposing the residue, after washing by decantation, with strong nitric acid, boiling after addition of water and filtering off the stannic acid. In spelter made by melting up old zinc several tenths per cent. of tin (from the solder) are frequently found.

Silicon, which seldom occurs in spelter, is determined in the same way as in aluminium. A large sample is dissolved in pure sodium hydroxide by warming in a platinum dish, the solution saturated with hydrochloric acid, evaporated to dryness, the silica rendered insoluble by prolonged heating of the residue to 150°, warmed with hydrochloric acid and water, the silica filtered off, washed with a large quantity of hot water, ignited, and, after weighing, treated with hydrofluoric acid and one drop of sulphuric acid, evaporated, the sulphuric acid evaporated off, the residue ignited, weighed, and the weight of pure silica estimated from the difference. $SiO_2 \times 0{\cdot}4693 = Si$.

(*c*) *Zinc Dust*.[1]—Zinc dust consists of an intimate mixture of finely divided metallic zinc (up to over 90 per cent.) and zinc oxide, together with some cadmium, iron, lead, arsenic, small particles of ore, and carbon. In commerce a product guaranteed to contain 90 per cent. of metal is usually demanded. The real content of metallic zinc can be arrived at only by a complete analysis. For the technical analysis the reducing action of the zinc on chromic acid, ferric salts, etc., is determined, or the volume of the hydrogen evolved on treatment with dilute acids is measured. Of the many methods proposed, that of Drewson[2] is frequently employed; it depends on the reduction of chromic acid to chromium oxide by the action of dilute sulphuric acid on zinc dust in presence of a measured quantity of a solution of potassium dichromate of known strength, and titrating back the excess of dichromate with a solution of ferrous sulphate. The equations representing the decompositions are:—

$$K_2Cr_2O_7 + 3Zn + 7H_2SO_4 = Cr_2(SO_4)_3 + 3ZnSO_4 + K_2SO_4 + 7H_2O,$$

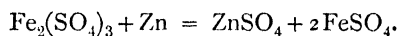
and $$K_2Cr_2O_7 + 6FeSO_4 + 8H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 2KHSO_4 + 7H_2O.$$

The potassium dichromate solution is prepared by dissolving 40 g. of the pure fused salt in 1 litre, and the ferrous sulphate solution by dissolving about 200 g. of the non-effloresced salt in 1 litre of dilute sulphuric acid (1 : 10). For determining the relation of the two solutions to one another, 20 c.c. of the iron solution is accurately measured out into a beaker, several c.c. of sulphuric acid and 50 c.c. of water added, and the dichromate solution run in from a burette until a drop of the iron solution when brought on to a drop of

[1] *Cf.* Edwards, *Chem. and Met. Eng.*, 1919, **21**, 192.
[2] *Z. anal. Chem.*, 1880, **19**, 50.

potassium ferricyanide on a porcelain plate shows no blue or green coloration. It is well to make a preliminary test with 20 c.c. of the iron solution by running in 1 c.c. of the dichromate solution at a time, stirring, taking a drop out, testing, etc., thereby arriving at the approximate amount of dichromate solution required; or this may be calculated from the equation if pure ferrous sulphate or ferrous ammonium sulphate is used.

For the determination, 0·5 g. of zinc dust is introduced into a beaker, 50 c.c. of the dichromate solution and 5 c.c. of dilute sulphuric acid (1 : 3) added, the mixture stirred round several times, a further 5 c.c. of dilute sulphuric acid added, and frequently stirred for a quarter of an hour. When all but a slight residue is dissolved, 100 c.c. of water, 10 c.c. of distilled sulphuric acid, and 25 c.c. of the ferrous sulphate solution are added, stirred round, and the ferrous sulphate solution run in from the burette, 1 c.c. at a time, stirring between each addition, until a drop of the solution gives a distinct blue coloration with the potassium ferricyanide. The solution is then titrated back with the dichromate solution until the blue colour disappears. From the total amount of dichromate solution used, the number of cubic centimetres corresponding to the added ferrous sulphate is deducted; the weight of potassium dichromate in the remaining amount of dichromate solution, multiplied by 0·6661, gives the content of metallic zinc. Since the small quantities of metallic iron and cadmium present also reduce corresponding quantities of chromic acid, the content of zinc always comes out too high.

A rapid method of valuation, due to Wahl, also depends on the reducing properties of zinc dust. One-half gram is shaken up with water till completely wetted, 15 g. of pure iron alum added, and again shaken; the ferric sulphate is reduced according to the equation:—

$$Fe_2(SO_4)_3 + Zn = ZnSO_4 + 2FeSO_4.$$

After the decomposition, 25 c.c. of sulphuric acid is added, the solution diluted, cooled, made up to 250 c.c., and the ferrous salt in 50 c.c. titrated with permanganate, after the addition of potassium fluoride or phosphoric acid. It is advisable to pass carbon dioxide through the flask during the decomposition.

R. Fresenius proposed to determine the content of zinc from the volume of hydrogen evolved on treatment with acids, a method which is most frequently used. F. Meyer[1] has described a special apparatus for this determination. An azotometer (Vol. I., p. 75), nitrometer (Vol. I. p. 78), or gas volumeter (Vol. I., p. 83) may also be employed. A simpler apparatus has been devised by O. Bach.[2] The

[1] *Z. angew. Chem.* 1894, 7, 231, 435; *J. Chem. Soc. Abstr.*, 1894, **66**, 332, 479.
[2] *Z. angew. Chem.*, 1894, 7, 291; *J. Chem. Soc. Abstr.*, 1894, **66**, 400.

volume of liberated hydrogen must be reduced to normal temperature and pressure and corrected for the presence of aqueous vapour. Taking the weight of 1 litre of hydrogen as 0·08998 g. and 65·37 as the atomic weight of zinc, the number of cubic centimetres of hydrogen evolved must be multiplied by 0·002918 in order to arrive at the weight of zinc contained in the zinc dust. It is to be borne in mind in these methods that the metallic impurities in the zinc dust (iron and cadmium) react like zinc itself.

3. For Alloys.

Alloys containing zinc (brass, etc.) are analysed by the methods given on pp. 220 *et seq.* Zinc alloyed with a little tin (up to 5 per cent.) is frequently used for castings. For the analysis, 1 to 2 g. is treated with strong nitric acid (which causes the tin oxide to separate in a more dense form than by using the usual acid of sp. gr. 1·2), 100 c.c. of boiling water added, boiled for five minutes, the stannic acid filtered off, and further treated as in the analysis of bronze (p. 216).

Alloys of zinc and aluminium[1] are analysed as follows:—One-half gram of the drillings is dissolved in a beaker in 25 c.c. of a 25 per cent. sodium hydroxide solution, the contents of the beaker warmed until rapid evolution of gas takes place, and then allowed to stand until solution is complete. The solution is diluted to 300 c.c. with boiling water, and any undissolved iron, copper, lead, tin, or nickel allowed to settle. The clear liquid, which contains nearly all the zinc and aluminium, is decanted, and the residue washed twice by decantation. This residue is dissolved in hydrochloric acid, diluted to 20 c.c., neutralised with sodium hydroxide (1 : 10), and 2 c.c. of the latter added in excess. After warming, the precipitated hydroxides are filtered off and the filtrate and washings added to the main bulk of solution. The zinc is then precipitated by means of sulphuretted hydrogen, the treatment being continued until alumina begins to be precipitated with the zinc sulphide; this point is easily recognised by the formation of a skin at the point where the bubbles of gas burst. The presence of a small amount of alumina (up to 10 per cent.) does not interfere with the ferrocyanide method of determination.[2] The zinc precipitate is allowed to settle, filtered, washed once only, dissolved in 8 c.c. of hydrochloric acid (1 : 10), the solution diluted to 250 c.c. with boiling water, 5 g. of ammonium chloride added, and the zinc determined by the ferrocyanide method.

Hard zinc, or zinc bottoms from the galvanising of iron, contain up to 6 per cent. of iron and several per cent. of lead. For their analysis several grams of turnings are warmed in a flask with a large excess

[1] R. Seligman and F. J. Willott, *J. Soc. Chem. Ind.*, 1905, **14**, 1278.
[2] Miller and Hall, *Columbia School of Mines Quarterly*, 1900, **21** (iii.), 267.

of dilute sulphuric acid (1 : 5) until the evolution of hydrogen ceases, the solution is decanted off from the separated spongy lead, cooled, and the contained iron titrated with permanganate. The lead is dissolved in a little nitric acid, the solution evaporated with sulphuric acid, and the lead determined in the usual way as lead sulphate.

4. For Waste Zinc and Ashes.

A large sample of waste zinc from the melting up of old zinc (fusion ashes), and of zinc ashes from the galvanising of iron (sal-ammoniac slags) is sieved into fine and coarse material, and the latter pounded in an iron mortar until the small pieces of metal are freed from the covering of oxide. The ground-up material is sieved, the coarse and the fine, together with the previously sieved material, weighed separately, and proportionate weighings of each taken so as to give a working sample of 10 g. The sample is dissolved in strong hydrochloric acid (for ashes rich in lead it is better to use nitric acid), and the solution made up to 1 litre without filtering. In 100 c.c. of this solution lead and copper are precipitated with sulphuretted hydrogen; the filtrate is boiled to expel the sulphuretted hydrogen, iron and manganese separated and the acidified solution titrated with potassium ferrocyanide (p. 297).

Determination of Chlorine in Sal-ammoniac Slags.—An average sample of 5 g. is shaken up for some time in the cold with a large excess of dilute nitric acid (one volume of acid of sp. gr. 1·2 diluted with one volume of water), the solution filtered into a 500 c.c. flask, the flask filled up to the mark, 100 c.c. of the solution taken, and precipitated with an excess of silver nitrate. The silver chloride is finally weighed as such and the content of chlorine calculated. $AgCl \times 0{\cdot}2474 = Cl$.

Zinc White Residues consist of coarse particles of zinc oxide together with a little metal and sand. One gram is dissolved in hot hydrochloric acid and a few drops of nitric acid, the solution saturated with ammonia, heated, filtered, and one-fifth of the filtrate titrated with sodium sulphide, or after acidifying with hydrochloric acid, with potassium ferrocyanide solution.

Residues and Flue dust are analysed in the same way as ores; flue dust generally contains considerable quantities of lead oxide, lead sulphate, etc., in addition to zinc oxide.

CADMIUM

Greenockite, CdS, is the most important of the few cadmium minerals known; it contains 77·6 per cent. of cadmium, is most frequently met with as a yellow earthy deposit on zinc blende, and is of no technical importance; cadmium is found much more frequently as sulphide or carbonate in zinc ores which contain from traces up to 0·3 and occasionally up to 0·8 per cent. The metal is prepared at zinc smelting works as a by-product in the production of zinc, from zinc fume, from the zinc dust collected in the early stages of the distillation, and from flue dust, and is purified by distillation.

Cadmium also occurs with zinc minerals in certain lead and copper ores and is recovered from the fume collected in bag houses through which the blast furnace gases are passed. The amount of cadmium present in the original ores is generally less than 0·1 per cent.[1]

I. Gravimetric Methods of Determination

1. Determination as Cadmium Sulphate.

When precipitated from moderately acid solutions with sulphuretted hydrogen, cadmium sulphide, if free from sulphur, may be collected on a weighed filter paper, and after drying at 100°, weighed as such. According to T. Fischer, it is precipitated quantitatively, free from zinc, from solutions which contain 10 c.c. of ordinary 25 per cent. hydrochloric acid (sp. gr. 1·125) and 1 g. of crystallised cadmium sulphate per 100 c.c. Cadmium is best determined as sulphate[2] by dissolving the cadmium sulphide in hot dilute nitric acid, evaporating the solution in a weighed crucible with a slight excess of sulphuric acid, driving off the sulphuric acid, and igniting the residue moderately strongly. $CdSO_4 \times 0{\cdot}5392 = Cd$. Cadmium may also be precipitated as hydroxide from pure solutions, ignited separately from the filter paper, and weighed as oxide.

Separation of Cadmium from other Metals (*cf.* also the Analysis of Commercial Lead, p. 234; Wood's Metal, p. 254; and Spelter, p. 301).—Any lead present is separated as sulphate; if the solution, containing ten to thirteen volumes per cent. of hydrochloric acid (see above) is precipitated with sulphuretted hydrogen and the washed precipitate treated with ammonium sulphide, only copper and bismuth are left to be separated from the cadmium. The sulphides are dissolved in

[1] *Cf.* N. F. Budgen, *Cadmium, its Metallurgy, Properties, and Uses.* London, 1924.

[2] *Cf.* also *Standard Methods of Chemical Analysis*, W. W. Scott, 1925, D. van Nostrand Company, New York.

hot, dilute nitric acid, the solution evaporated, the bismuth separated as oxychloride, cadmium and copper precipitated in the filtrate from the bismuth oxychloride with sulphuretted hydrogen, and small quantities of copper dissolved out of the precipitate by means of warm potassium cyanide solution. If much copper is present, the precipitate is dissolved in nitric acid, the solution evaporated, and the copper deposited electrolytically from the solution containing over 5 per cent. of sulphuric acid; or, the nitric acid solution is neutralised with potassium or sodium hydroxide, warmed with an excess of potassium cyanide, the cadmium precipitated as sulphide by the addition of a little ammonium sulphide solution, and finally estimated as cadmium sulphate. Cadmium is separated from large quantities of zinc, and smaller quantities of iron and manganese (solutions of ores) by warming the solution, after the separation of the lead as sulphate, with a good excess of sodium hydroxide, diluting, cooling, filtering, washing the precipitate with water containing some sodium hydroxide, extracting the cadmium hydroxide, with ammonia, neutralising the ammoniacal solution, adding ten volumes per cent. of hydrochloric acid, passing in sulphuretted hydrogen, in the cold, and thus precipitating pure cadmium sulphide, which is converted into sulphate. In solutions of common calamine containing much iron and aluminium, the lead is separated, the filtrate treated with sulphuretted hydrogen, the cadmium sulphide containing zinc sulphide dissolved in a measured quantity of hot hydrochloric acid, the solution diluted until it contains ten volumes per cent. of hydrochloric acid, and then pure cadmium sulphide precipitated by means of sulphuretted hydrogen.

2. Electrolytic Determination of Cadmium.

Cadmium may be determined electrolytically from its solution in various electrolytes. A potassium cyanide solution is very largely used for this purpose. The cadmium from 1 g. of ore is first obtained as chloride or sulphate solution free from other metals, precipitated in acid solution by sulphuretted hydrogen, and the solution evaporated, if necessary, to 100 c.c. or less. A few drops of phenolphthalein solution are added, and then pure sodium or potassium hydroxide solution, until a permanent red colour is obtained. A concentrated solution of pure potassium cyanide is then added until the precipitated cadmium hydroxide is completely dissolved; an excess must be avoided. The solution is diluted to 100 to 125 c.c., heated to 60°, and electrolysed with a current of ND_{100} = 0·04 to 0·06 ampère at 2·9 to 3·2 volts. The deposition is usually complete in from four to six hours; when finished, the electrode is washed with hot water, then with alcohol, and finally

dried at 100° and weighed. The deposition can also be effected from a sulphate solution,[1] and rapid deposition accomplished by means of a rotating anode used at 600 revolutions per minute.

II. Volumetric Method

A cadmium sulphide precipitate is frequently titrated with iodine in the determination of sulphur in iron and steel by the evolution method, and this process may also be used in the determination of cadmium.[2]

The cadmium sulphide after separation from other sulphides, as already described, is filtered and washed; the filter paper containing the precipitate is transferred to a beaker, a slight excess of hydrochloric acid is added and the solution titrated with N/10 iodine solution, starch solution being added towards the end of the titration as an indicator. One c.c. N/10 iodine = 0·00562 g. cadmium (*cf.* p. 58).

An alternative method of carrying out the titration is to add excess of the iodine solution and titrate back with standard thiosulphate solution.

III. Analysis of Zinc Ores and of Metallurgical Products containing Cadmium

Ores, Zinc fume, and Flue dust.—W. Minor[3] dissolves ores, etc., in hydrochloric acid or aqua regia; the solution is evaporated with excess of sulphuric acid to separate the lead, filtered, and sulphuretted hydrogen passed into the filtrate, whereby cadmium sulphide containing zinc sulphide is precipitated. The precipitate is dissolved in hot hydrochloric acid, the sulphuretted hydrogen driven off, hot sodium hydroxide solution added, the solution boiled, the cadmium hydroxide filtered off, washed first with 1 per cent. sodium hydroxide solution then with hot water, dried, the filter paper ashed in a Rose's crucible at a moderate heat, the lid placed on, and oxygen led into the crucible, which is ignited to a dull red heat. The cadmium oxide remaining is weighed. $CdO \times 0{\cdot}8754 = Cd$. If the filter ash is heated too strongly, some cadmium may volatilise; it is better, therefore, to dissolve the washed hydroxide in hot, dilute hydrochloric acid, evaporate the solution down in a weighed porcelain crucible with a slight excess of sulphuric acid, and estimate the cadmium as sulphate (p. 307).

If sodium thiosulphate is added to a hot hydrochloric or sulphuric acid solution of a zinc ore and the solution boiled, no cadmium sulphide is precipitated.

[1] *Cf.* E. F. Smith, *Electro-Analysis*, p. 82; and Kallock and Smith, *J. Amer. Chem. Soc.*, 1899, **21**, 925.

[2] W. W. Scott, *Standard Methods of Chemical Analysis*, 1927, pp. 103, 501, 686.

[3] *Chem. Zeit.*, 1890, **14**, 4, 34, 348; *J. Chem. Soc. Abstr.*, 1891, **60**, 112.

Zinc dust.—An average sample of from 20 to 40 g. is dissolved in a moderate excess of hydrochloric acid, the solution filtered, 50 or 100 c.c. of the filtrate (made up to 1 or 2 litres) taken, diluted to 300 to 500 c.c., sulphuretted hydrogen passed in, the precipitated cadmium sulphide, containing zinc, dissolved in a measured quantity of hot hydrochloric acid, the solution diluted so as to contain ten volumes per cent. of hydrochloric acid, pure cadmium sulphide precipitated with sulphuretted hydrogen, and weighed as sulphate as above. According to J. J. Fox[1] the presence of trichloracetic acid avoids the necessity for reprecipitation.

Crude Zinc and Spelter.[2]—An average sample of 25 g. is warmed with insufficient dilute hydrochloric acid to effect complete solution, the solution decanted off, the residue containing all the cadmium and lead is dissolved in dilute nitric acid, the solution evaporated with a slight excess of sulphuric acid, the residue taken up with water, and the lead sulphate filtered off; 10 g. ammonium chloride is added to the filtrate, sulphuretted hydrogen passed in and the precipitate filtered off. This impure precipitate is dissolved by boiling in dilute sulphuric acid (1 : 5), the solution diluted proportionately and cadmium sulphide again precipitated by means of sulphuretted hydrogen. The cadmium sulphide is dissolved in dilute hydrochloric acid (1 : 3) and the solution is evaporated with sulphuric acid and the cadmium sulphate weighed.

IV. Metallic Cadmium

The commercial metal generally contains over 99·5 per cent. of cadmium; the chief impurities are zinc, a little lead, iron, and copper, and sometimes tin, arsenic, nickel, and thallium.

For the analysis, 2 g. is dissolved in a covered dish by warming with 50 c.c. of 10 per cent. sulphuric acid with the addition of some nitric acid, the solution evaporated, the residue taken up with water, the lead sulphate filtered off, and the copper deposited electrolytically from the filtrate in a large platinum crucible. The solution, freed from copper, is diluted in a beaker to about 400 c.c., 40 c.c. of hydrochloric acid (sp. gr. 1·125) added, sulphuretted hydrogen passed in for a long time, until all the cadmium is precipitated as sulphide, which is filtered off and washed with dilute sulphuretted hydrogen water containing ten volumes per cent. of hydrochloric acid. The filtrate from the cadmium sulphide is evaporated to drive off the hydrochloric acid and most of the sulphuric acid, the cooled residue taken up with water, and a slight excess of sodium carbonate added. The solution is boiled for ten

[1] *J. Chem. Soc.*, 1907, 91, 964.

[2] Standard method of American Society for Testing Materials, *Ind. Eng. Chem.*, 1915, 7, 547.

minutes, the zinc carbonate containing iron filtered off and washed with hot water; the filter paper is dried and the contents of the paper removed as completely as possible. The paper is then ignited in a weighed porcelain crucible, the zinc carbonate transferred to the crucible, ignited, and weighed. After weighing, the impure zinc oxide is dissolved in hydrochloric acid, the solution diluted, warmed to 70°, potassium iodide added, cooled, and the free iodine titrated in presence of starch with a standard solution of sodium thiosulphate. The iron so determined is deducted, as Fe_2O_3, from the weight of impure zinc oxide.

V. Cadmium Alloys

The fusible alloys containing cadmium are analysed in the same way as Wood's metal (*cf.* Bismuth, p. 254). In the analysis of the cadmium amalgams occasionally used in dentistry, the mercury cannot be determined by distillation on account of the volatility of cadmium. One gram of the amalgam is dissolved in nitric acid, the solution evaporated, the residue taken up with dilute hydrochloric acid, the mercury precipitated as mercurous chloride with phosphorous acid (phosphorus trichloride and water), and after diluting the filtrate with water, the cadmium is precipitated as sulphide by passing in sulphuretted hydrogen, etc.

The most important alloys of cadmium are those with copper, containing about one per cent. of cadmium and used for telegraph, telephone, and power transmission wires. Five g. of alloy is dissolved in nitric acid, evaporated to dryness, taken up with water and made just alkaline with ammonium carbonate. Potassium cyanide solution is now added until the solution is colourless and sulphuretted hydrogen passed to precipitate the cadmium. The cadmium sulphide precipitate is purified and the determination may be completed gravimetrically as sulphate, electrolytically, or volumetrically by means of iodine.

ALUMINIUM

Commercial aluminium always contains some silicon, iron, and a little copper as impurities; other impurities present are: carbon, nitrogen, sodium, lead, and traces of antimony, phosphorus, and sulphur. Sodium always appears among the constituents specified by Government departments as not allowable beyond a trace (0·05 per cent., reduced afterwards to 0·03 per cent.).

A. TECHNICAL ANALYSIS OF ALUMINIUM[1]

I. Usual Method of Analysis.

This is restricted to the determination of the silicon, iron, copper, and sodium.

1. *Total Silicon.*—One to three grams of metallic turnings are treated in a roomy, covered platinum dish with five to six times the weight of chemically pure sodium hydroxide[2] dissolved in 25 to 75 c.c. of water. After the first violent reaction is over, the contents of the dish are gently warmed, the cover-glass (a platinum cover is better) washed, hydrochloric acid added in excess, the solution evaporated, the silica rendered insoluble in the usual way, the residue dissolved by warming with hydrochloric acid and water, the solution cooled, the silica filtered off, and ignited in a platinum crucible. After weighing, the result is checked by treating the contents of the crucible on the water-bath with a few cubic centimetres of hydrofluoric acid and one drop of sulphuric acid, the solution evaporated, the sulphuric acid carefully driven off, and the residue strongly ignited and weighed.

The difference between the two weighings is silica. $SiO_2 \times 0{\cdot}4693 =$ Silicon.

The copper in the filtrate from the silica, precipitated as sulphide by passing in sulphuretted hydrogen, is filtered off, dissolved in a little hot nitric acid, and the copper in the solution either titrated or determined colorimetrically (*cf.* pp. 187-190). The iron may be determined by titration with potassium permanganate in the filtrate from the copper sulphide, after boiling the solution for half an hour to remove the sulphuretted hydrogen, largely diluting the cooled solution, and adding several c.c. of sulphuric acid, and about 5 to 10 g. of crystallised sodium sulphate.

For the determination of the silicon, O. Handy[3] dissolves the turnings in a mixture of 100 c.c. of nitric acid[4] (sp. gr. 1·42), 300 c.c. of hydrochloric acid (sp. gr. 1·2) and 600 c.c. of 25 per cent. sulphuric acid; by the use of this acid mixture, none of the silicon is evolved as hydride. One gram of the metal is treated in a covered porcelain dish with 20 to 30 c.c. of the acid mixture, gently warmed until the metal is completely attacked, the solution evaporated, and the residue heated until fumes of sulphuric acid are evolved. The cooled residue is next warmed for some time with 100 c.c. of 25 per cent. sulphuric

[1] *Cf.* R. Seligman and F. J. Willott, *J. Inst. Metals*, 1910, **3**, 138.

[2] Regelsberger, "Valuation of Aluminium and its Alloys," *Z. angew. Chem.*, 1891, **4**, 442, 473; *J. Chem. Soc. Abstr.*, 1893, **64**, 48.

[3] *J. Amer. Chem. Soc.*, 1896, **18**, 766; *J. Chem. Soc. Abstr.*, 1897, **72**, 191.

[4] *Cf.* Moissan, *Comptes rend.*, 1905, **121**, 851; Sibbers, *Pharm. Zeit.*, 1907, **42**, 622.

acid; 100 c.c. of boiling water is then added, the sulphate completely dissolved by boiling, the mixture of silica and silicon filtered off, the filter paper ignited in a platinum crucible, the residue fused with 1 g. of sodium carbonate, the silica separated from the fused mass in the usual way (decomposition with hydrochloric or sulphuric acid, evaporation, etc.), weighed, and its purity determined by evaporating with hydrofluoric acid, etc., as above. The silica thus found represents the total silicon content.

2. *Graphitic* (*crystalline*) *Silicon.*—The mixture of silica and silicon obtained as above from a separate weighing is treated in a platinum crucible with several cubic centimetres of hydrofluoric acid and one drop of sulphuric acid, the solution evaporated, the sulphuric acid driven off, the brown residue (silicon) strongly ignited and weighed, after half an hour. The difference between the weight of silicon thus found and the weight of total silicon estimated previously gives the content of combined silicon.[1]

3. *Iron.*—According to O. Handy, 1 g. of the metal is dissolved in 20 to 30 c.c. of the acid mixture described above (1), the solution evaporated until sulphuric acid fumes are copiously evolved, the residue taken up by warming with dilute sulphuric acid, the ferric sulphate in the solution reduced by 1 g. of pure zinc, and the cooled, diluted solution titrated with potassium permanganate.

Regelsberger[2] dissolves 3 g. of turnings in a 500 c.c. flask in a sufficient quantity of 30 to 50 per cent. potassium hydroxide, finally warming, adds 200 c.c. of dilute sulphuric acid (sp. gr. 1·16) with shaking, boils until the solution clears, cools, and titrates with permanganate.

4. *Copper.*—One gram of turnings are treated in a platinum dish with 5 g. of sodium hydroxide and 25 c.c. of water, the solution diluted, the residue consisting of copper and iron filtered off and well washed, dissolved in a few c.c. of hot, dilute nitric acid, the iron precipitated by adding excess of ammonia, the ferric hydroxide filtered off, and the copper in the filtrate determined colorimetrically (*cf.* p. 187). When there is a large content of copper it is determined by electrolysis.

5. *Sodium.*—Many methods have been suggested for the determination of sodium, that of Moissan[3] probably being the best known. This consists in the solution of the sample in nitric acid (with the addition of a few drops of mercuric chloride to assist the reaction), evaporating the solution in a platinum dish, decomposing the aluminium nitrate[4] by heating, extracting the sodium salts, purifying and weighing.

[1] *Cf.* Hunt, Clapp, and Handy, *Chem. News*, 1902, **65**, 223, 235.
[2] *Loc. cit.*
[3] *Compt. rend.*, 1895, **121**, 851; *J. Soc. Chem. Ind.*, 1896, **15**, 136.
[4] Deville, *Ann. Chim. Phys.*, 1853, **3**, 38.

Other methods include the volatilisation of the aluminium by heating in various gases (chlorine, hydrochloric acid, etc.); solution of the aluminium in various reagents which leave the sodium in a relatively small residue as in the method of Gulewitsch[1] in which a mixture of benzene and mercuric chloride is used or the method in which ether, saturated with hydrochloric acid, is employed.

D. M. Fairlie and G. B. Brook[2] have made a thorough examination of the methods available, and as a result of their work recommend the following:—

Into an 8-inch quartz basin which has been previously weighed on a rough balance, 250 c.c. distilled water and 10 c.c. saturated mercuric chloride solution are placed, after which 30 g. of fine aluminium millings are added and the whole warmed until reaction commences. Nitric acid (70 per cent.) is added a small quantity at a time up to 400 c.c., and if the mass becomes viscous, a further 100 c.c. of water is added. The solution is evaporated until it weighs approximately 600 g. and then cooled with constant stirring and placing the dish in a water bath. After standing for an hour or so the crystals are filtered off, using a 6-inch Hirsch porcelain funnel with a suitable arrangement for applying suction, the crystals pressed well with a quartz rod, sucked dry, and finally washed with 50 c.c. of nitric acid (70 per cent.).

The filtrate and washings are evaporated until a hot saturated solution is obtained which is allowed to crystallise. The solution is filtered through a 7 cm. funnel with a platinum filter cone and the crystals washed with 5 c.c. nitric acid (70 per cent.). The filtrate is collected in a 3¼ in. quartz basin, 2 c.c. of concentrated sulphuric acid added, the whole evaporated slowly to fumes and baked until white fumes cease to be evolved. After cooling 10 c.c. of strong ammonium hydroxide is added, mixed in well with a quartz rod and allowed to stand overnight, covered with a bell-jar to prevent access of dust. The solution is next warmed, filtered through a small filter paper (1 in. in diameter) into a weighed platinum basin and the residue washed with hot water.

After the addition of 0·5 c.c. of sulphuric acid, the solution is evaporated to dryness and the residue ignited. Two c.c. of saturated ammonium carbonate solution is added to the residue, which is again taken to dryness, ignited, and weighed. The weighed residue is digested with a few c.c. of hot water and filtered through a small paper; the paper is transferred to the dish, ignited and again weighed. This weight is subtracted from the weight of the first ignited residue and gives the weight of impure sodium sulphate.

[1] *J. Soc. Chem. Ind.*, 1904, **23**, 627.
[2] *J. Inst. Metals*, 1924, **32**, 283.

The last filtrate obtained is tested by the usual group reagents and the weight of any impurities (*e.g.*, a trace of iron, aluminium or magnesium) found is deducted from the weight of the impure sodium sulphate. From the weight finally obtained the blank on the reagents must be deducted and the sodium calculated from the sodium sulphate obtained. Blanks should be run alongside every three or four determinations and usually yield sodium sulphate equivalent to 0·003 per cent. sodium in the metal. All apparatus used in the process should be kept apart and never used for other purposes.

The method as described extracts about 90 per cent. of the sodium present. For special purposes, a second crystallisation is carried out, the crystals from the first treatment being heated up with 150 c.c. nitric acid and allowed to recrystallise, the mother liquor being added either to the original mother liquor or treated separately.

2. More Complete Analysis.

This includes the determination of aluminium, carbon, lead, phosphorus, sulphur, arsenic, and nitrogen.

1. *Aluminium.*—One to five grams of an average sample is dissolved in a large flask in very dilute hydrochloric acid (1 : 5), finally warming, sulphuretted hydrogen passed in after cooling, the solution filtered into a measuring flask, and the filter paper and precipitate washed with water containing dilute hydrochloric acid and sulphuretted hydrogen water. After filling up to the mark, a volume of the solution corresponding to 0·2 g. of the sample is withdrawn with a pipette, the solution run into a large platinum dish, the sulphuretted hydrogen driven off by heating, and the iron in the solution oxidised with a few drops of bromine water. The solution is then diluted to 200 to 300 c.c., excess of ammonia added, the dish covered, the contents boiled until the ammonia is completely expelled, the precipitate filtered off, washed with boiling water until the runnings cease to give a chloride reaction, the impure aluminium hydroxide dried, ignited over the blowpipe and weighed. The iron is determined in a separate analysis, and is deducted as ferric oxide (*cf.* p. 313). $Al_2O_3 \times 0{\cdot}5303$ = Aluminium.

In general practice it is unusual to determine the amount of aluminium present, the impurities only being determined and the aluminium obtained by difference.

2. *Carbon.*—Regelsberger[1] recommends direct combustion in the wet way by means of chromic and sulphuric acids; Corleis's apparatus (*cf.* pp. 41 *et seq.*) is specially suitable for the determination.

H. Moissan treats 10 g. of aluminium with concentrated potassium hydroxide solution, thoroughly washes the residue containing the

[1] *Loc. cit.*

carbon on an asbestos filter, dries in a porcelain boat, oxidises the carbon in a current of oxygen, and collects the carbon dioxide in potash bulbs. According to Moissan, aluminium contains only combined carbon; he found from 0·08 to 0·104 per cent. in various samples.

Moissan, Gouthière, and others also recommend the separation of the carbon by means of mercuric chloride, according to Boussingault's method.

3. *Lead.*—If the aluminium is dissolved, etc., by Handy's method (p. 312), the lead will be found as sulphate, together with the mixture of silica and silicon. The lead sulphate is extracted with a hot solution of ammonium acetate, and precipitated from the acetate solution either by sulphuretted hydrogen or by potassium chromate.

4. *Phosphorus*, *Sulphur*, and *Arsenic* are determined, according to M. Jean,[1] by dissolving 10 g. of the metal in very dilute hydrochloric acid and passing the impure hydrogen evolved into bromine water (*cf.* Determination of Sulphur in Iron, p. 57). The solution in the receiver is divided into two portions; the sulphur is determined as barium sulphate, the arsenic by precipitation with sulphuretted hydrogen, etc., and in the filtrate from the arsenic sulphide the phosphoric acid by means of ammonium molybdate solution. H. Gouthière[2] determines the sulphur by igniting several grams of the finely divided metal in a current of pure hydrogen, passing the hydrogen through an ammoniacal solution of silver, filtering off the precipitated silver sulphide, washing, drying, igniting, and weighing as metallic silver. $Ag \times 0{\cdot}1486 = $ Sulphur.

5. *Nitrogen.*—Moissan dissolves a somewhat large sample in pure 10 per cent. potassium hydroxide, distils off the ammonia formed into dilute hydrochloric acid, and estimates it colorimetrically with Nessler's solution.

B. Aluminium Alloys[3]

Aluminium is frequently alloyed with copper alone or with copper and about 1 per cent. of manganese. Other aluminium alloys contain copper together with small quantities of iron, zinc, nickel or magnesium, and an important class contain zinc and copper together with one or more of the following metals in small amounts: tin, iron, nickel, manganese, magnesium; aluminium—silicon alloys are also favoured for certain classes of work.

1. Aluminium with Copper.—Copper may be present in varying amounts with or without other metals.

[1] Campredon, *Guide pratique du Chimiste Metallurgiste*, p. 271.

[2] *Ann. Chim. anal.*, 1 [14], 265; *J. Soc. Chem. Ind.*, 1896, **15**, 830.

[3] *Cf.* W. H. Withey, *J. Inst. Metals*, 1916, **15**, 207; J. H. Stansbie, *J. Soc. Chem. Ind.*, 1917, **36**, 802; B. Collitt and W. Regan, *J. Soc. Chem. Ind.*, 1918, **37**, 91 T.

One gram of fine drillings is treated with 30 c.c. of a 15 per cent. solution of sodium hydroxide. After dilution and boiling, the residue is filtered, washed, and dissolved in hot, dilute nitric acid, and the copper deposited from the solution electrolytically. Alloys containing more than 8 per cent. of copper may be dissolved in dilute nitric acid, the solution evaporated with excess of sulphuric acid, the residue taken up with water, the silica filtered off, and the filtrate electrolysed.

The solution of copper in nitric acid obtained by either of these methods may alternatively be evaporated to a low bulk, diluted slightly, 5 c.c. of dilute ammonium hydroxide added and boiled. After cooling, 6 c.c. of glacial acetic acid is added, then 50 c.c. of sodium fluoride solution followed by 10 to 15 c.c. of potassium iodide solution (25 g. in 100 c.c.). The solution is now ready for titration with standard sodium thiosulphate solution, using starch as an indicator.

2. **Aluminium with Nickel and Copper.**—Aluminium is alloyed with up to 2 per cent. of nickel, and at the same time copper and magnesium are generally added.

One to five grams of turnings are decomposed as described under 1, the copper deposited electrolytically from the nitrate solution, the solution from the copper evaporated with excess of sulphuric acid until fumes of sulphuric acid begin to be evolved, the cooled residue dissolved in 20 to 50 c.c. of water, a large excess of ammonia added, and the nickel separated electrolytically.

The nickel may be determined by the dimethylglyoxime method (p. 66), when the residue from sodium hydroxide treatment is dissolved in 20 c.c. of hydrochloric acid (sp. gr. 1·16) and 5 c.c. of nitric acid (sp. gr. 1·42), the solution is boiled, diluted, filtered, and the precipitate washed with hot water and hot dilute hydrochloric acid. Six grams of tartaric acid is added, the solution diluted to 400 c.c., made slightly alkaline with ammonium hydroxide and then faintly acid with hydrochloric acid. Thirty c.c. of alcoholic solution of dimethylglyoxime (1 per cent.) is added and then ammonia drop by drop until the solution is faintly alkaline. The solution is allowed to stand for one hour in a warm place, then filtered and the precipitate washed, dried and weighed.

3. **Aluminium with Manganese and Copper.**—When the copper has been determined by electrolysis (Method 1 above) the solution, after the deposition of copper, may be used for the determination of manganese. One to two grams of sodium bismuthate is added to the solution which is well shaken for three or four minutes. It is allowed to settle and filtered through an ignited asbestos filter and well washed with a 2 per cent. nitric acid solution. A measured quantity of standard ferrous ammonium sulphate is now added and the excess titrated back by means of permanganate solution.

An alternative method for determining manganese consists of decomposing 1 g. by means of sodium hydroxide as in Method 1, cooling, adding 90 c.c. of nitric acid (sp. gr. 1·18), and boiling until all nitrous fumes are expelled. The solution after cooling is made up to 250 c.c., thoroughly mixed, and 50 c.c. (0·2 g. alloy) is pipetted off into a 300 c.c. conical flask. Twenty-five c.c. of silver nitrate solution (2 g. per litre) is added and the solution heated to boiling. Five c.c. of ammonium persulphate solution (15 per cent.) is now added, the flask immersed in boiling water for one minute, cooled, 80 c.c. of cold distilled water added, and the solution titrated with a standard solution of sodium arsenite.

4. **Aluminium with Zinc.**—Upon decomposing aluminium alloys with sodium hydroxide solution any zinc present passes into solution; but if copper, iron, and other metals insoluble in the alkali solution are present some zinc may remain undissolved.

The solution obtained from 1 or 2 g. of alloy may be subjected to electrolysis using a weighed copper cathode and a current of 0·6 to 0·7 amperes for forty-five minutes with one electrode rotating. The deposit should be well washed with cold water, then dipped into alcohol, dried, and weighed.

An alternative method consists in precipitating zinc as sulphide from the alkaline solution by means of sulphuretted hydrogen or a few crystals of sodium sulphide. A better result may be obtained by slightly acidifying the solution with sulphuric acid and adding a small quantity of sulphurous acid before gassing with sulphuretted hydrogen. The precipitate is filtered, washed, dissolved in hydrochloric acid and determined volumetrically by titration with potassium ferrocyanide solution or gravimetrically by precipitation as zinc ammonium phosphate, which is filtered off, washed, ignited and weighed as zinc pyrophosphate.

In the event of zinc being retained in the undissolved metals it is advisable to add a few crystals of sodium sulphide to the alkali solution, filter off the residue and zinc sulphide precipitate, wash once or twice with hot water, dissolve in nitrohydrochloric acid and then proceed to the separation and determination of copper, iron, manganese and zinc.

5. **Aluminium with Magnesium.**—Alloys such as "Magnalium," etc., known as Light Alloys, are largely used at the present time and contain magnesium.

On decomposing aluminium alloys with sodium hydroxide solution, any magnesium present remains with the insoluble residue together with copper, etc., as mentioned above.

For the determination of magnesium, 2 g. of the alloy is treated with 100 c.c. sodium hydroxide solution (15 per cent.) then diluted to 300 c.c. with hot water and boiled. The residue is filtered, washed

with hot water, and dissolved in 20 c.c. of a mixture of equal parts of hydrochloric acid (sp. gr. 1·16) and nitric acid (sp. gr. 1·42). The solution is diluted and filtered, the bulk of the filtrate and washings being kept small. Ten c.c. of concentrated sulphuric acid is added and the solution evaporated to fumes. After cooling, 200 c.c. of hot water is added and the copper precipitated by means of a rapid stream of sulphuretted hydrogen and filtered. The filtrate is boiled until free from sulphuretted hydrogen and a few drops of bromine added to oxidise the iron and manganese present. Three grams of ammonium chloride is added and a slight excess of ammonium hydroxide solution. The iron-aluminium-manganese precipitate is filtered off, well washed, and is used for the determination of iron and manganese.

To the filtrate from the mixed hydroxides, which should be practically neutral, 0·5 c.c. ammonium hydroxide solution is added, the whole heated to 70° and saturated with sulphuretted hydrogen, after which the precipitated sulphides are filtered off and washed. The filtrate is acidified, evaporated somewhat, nitric acid added and the solution evaporated to a small bulk. Any precipitated sulphur is filtered off and washed. Twenty c.c. of ammonium phosphate solution is next added, the solution neutralised with ammonia, and then more of the ammonium hydroxide solution (sp. gr. 0·9) is gradually added with constantly stirring until the latter forms one-third of the total volume.

The solution is stirred at intervals, allowed to stand twelve hours, filtered, the precipitate washed with dilute ammonia, dried, ignited gently at first and afterwards strongly, and weighed as magnesium pyrophosphate.

6. Aluminium with Silicon.—One gram of the alloy is treated with 15 c.c. of water, 6 c.c. of concentrated sulphuric acid and 5 c.c. of strong nitric acid, allowed to digest for a moderate period on the cooler part of the hot plate and eventually evaporated to fumes. After cooling, 50 c.c. of water is added, the silica filtered off, washed thoroughly with hot water, ignited in a tared platinum crucible and weighed. As the silica may be impure it is treated with hydrofluoric acid in the usual way and the weight of the residue deducted from the first weight.

7. Iron-Aluminium Alloys (Ferro-aluminium and Ferro-silicon-aluminium).

These alloys contain up to 15 per cent. of aluminium (generally 10 per cent.) and up to 15 per cent. of silicon; they are used in large quantities as additions to cast iron and for the deoxidation of steel. The content of aluminium is best determined either by J. Rothe's ether-separation method (*cf.* Iron, p. 6), or by Baudisch's "Cupferron" method (p. 82).

NICKEL AND COBALT

These metals, which are so very similar in their chemical behaviour, are always found associated together, both in their ores and in the metallurgical products produced therefrom. Ores poor in copper yield good results when carefully assayed by Plattner's dry methods.[1] For the accurate determination of nickel, cobalt, and the other associated metals, and of the impurities, gravimetric and volumetric methods are employed, and the two metals themselves are frequently deposited together electrolytically.

Ores.—The most important ores are:—

Niccolite or *Kupfernickel*, NiAs, containing 43·5 per cent. of nickel; in many varieties the arsenic is largely replaced (up to 28 per cent.) by antimony.

Chloranthite, $NiAs_2$, containing 28·2 per cent. of nickel; nickel is frequently replaced by cobalt and iron (up to 17 per cent. iron).

Millerite or *Nickel Blende*, NiS, containing 64·5 per cent. of nickel.

Pentlandite, (FeNi)S, containing 40 per cent. of nickel.

Antimonial Nickel, NiSb, containing 32·2 per cent. of nickel. *Antimonial Nickel Ore*, *Ullmanite*, NiSbS, containing 27·35 per cent. of nickel. *Arsenical Nickel Ore*, NiAsS, containing 35·15 per cent. of nickel.

Nickel Magnesium Silicates, containing water. *Rewdanskite*, containing up to 18 per cent. of nickel. *Garnierite*, with up to 30 per cent. of nickel; and many similar silicates containing nickel.

Magnetic pyrites, *Iron pyrites*, and *Copper pyrites*, containing nickel, are found in large quantities, especially in the Sudbury district of Ontario where the ore contains about 3 per cent. nickel, 1·5 per cent. copper, and an appreciable amount of gold, silver, and the platinum metals.

Smaltite, $CoAs_2$, when pure containing 28 per cent. of cobalt, very requently containing considerable quantities of iron and nickel.

Cobaltite, CoAsS, containing 35·5 per cent. of cobalt, frequently with a high content of iron.

Cobalt Nickel Blende, 2RS, $3R_2S_3$ (R = Ni, Co, Fe), containing 11 to 40·7 per cent. of cobalt and 14·6 to 42·6 per cent. of nickel.

Earthy Cobalt or *Wad* (Co,Mn)O, $2MnO_2$ $4H_2O$, containing up to 15 per cent. of cobalt.

[1] *Cf.* Kerl, *Metallurgische Probierkunst*, 2nd ed., and *Probierbuch*, 3rd ed.; also Ricketts and Miller, *Notes on Assaying*, 3rd ed., 1902, p. 84.

A. SEPARATION OF NICKEL AND COBALT FROM OTHER METALS

Finely ground ores, speisses, and mattes are dissolved in a flask by warming with aqua regia (20 c.c. for 1 g. of substance), the solution boiled, the residue evaporated to dryness with hydrochloric acid, taken up again with dilute hydrochloric acid, and arsenic, antimony, copper, lead, bismuth, etc., precipitated by passing sulphuretted hydrogen for some time into the gently warmed solution. The solution of arsenical ores and speisses is repeatedly boiled with additions of sulphurous acid so as to reduce all arsenic oxide to arsenious oxide, before treatment with sulphuretted hydrogen ; a previous roasting of such substances is also to be recommended, whereby the greater part of any arsenic and sulphur present is removed. The powdered substance, spread out on a scorifying dish, is first roasted in a muffle to a dull red heat, the cooled, roasted material then mixed with an equal volume of powdered wood charcoal, the roasting again carried out at a higher temperature, and again repeated.

Pyrites and mattes poor in nickel and cobalt are also first roasted "sweet," if it is desired to treat their solution by Rothe's method, p. 6.

For the determination of any zinc present, the sulphuretted hydrogen in the filtrate from the sulphide precipitates is boiled off, bromine water added, the cooled solution nearly neutralised in the presence of a few drops of Congo red solution, and the zinc precipitated as sulphide by passing in sulphuretted hydrogen for a long time (*cf.* p. 293). The filtrate from the zinc sulphide is evaporated over a free flame, the iron oxidised in the concentrated solution with a little nitric acid, the cooled solution neutralised with sodium hydroxide or sodium carbonate solution, sodium acetate (six times the weight of the suspected iron content) added, the solution largely diluted with water, heated to boiling, and boiled for five minutes. The bulky precipitate containing all the iron and aluminium as basic acetates is filtered off and washed with hot water. Since the precipitate always retains some nickel and cobalt, it must be dissolved at least once and reprecipitated by boiling with sodium acetate after neutralisation; if the substance contains much iron, nickel may be detected in the filtrate after reprecipitating four times. The combined filtrates are heated in a porcelain dish, and sodium hydroxide and bromine water added in excess. After the dark brown precipitate containing all the nickel, cobalt, and manganese has separated out, it is filtered off, washed with hot water, dissolved in hot, dilute sulphuric acid to which some sulphurous acid is added, and the solution evaporated on the water-bath. If the manganese present does not

amount to more than a few per cent., the solution is washed into a beaker of 200 c.c. capacity, a large excess of ammonia (30 to 50 c.c.) added, together with 30 c.c. of a cold, saturated solution of ammonium sulphate,[1] the solution of about 150 c.c. stirred, a platinum cone and spiral placed in the beaker, and the nickel and cobalt deposited electrolytically by means of a current of 2·8 to 3·3 volts and 0·5 to 1·5 ampères per 100 sq. cm. of cathode surface, at the ordinary temperature. All the manganese separates as hydrated manganese dioxide, which floats about as a flocculent precipitate in the liquid and only adheres to the spiral to a very slight extent.

Copper or nickel gauze cathodes are commonly used for the deposition of nickel and cobalt.

A higher percentage of manganese interferes with the electrolysis. The solution containing the sulphates of nickel, cobalt, and manganese (see above) is then washed into a pressure-bottle of about 500 c.c. capacity, neutralised with ammonia, 30 c.c. of a solution of ammonium acetate, prepared by neutralising acetic acid with ammonia, and 20 c.c. of 50 per cent. acetic acid added, diluted to 300 to 400 c.c., sulphuretted hydrogen passed in for from one to two hours, the stopper screwed down, the bottle placed in a cold water bath, and this latter heated to boiling within half an hour. Nickel and cobalt separate as black sulphides, which adhere to some extent to the sides of the bottle. The bottle is allowed to cool to about 50° in the water bath, then taken out, the stopper removed, the sulphides filtered off, washed with water to which some acetic acid and sulphuretted hydrogen water is added, the sulphides washed off the filter paper into a porcelain dish, and the water evaporated off. The filter paper is ignited and the ash added to the contents of the dish, in which (after covering with a clock-glass) the sulphides of nickel and cobalt are dissolved by warming with strong nitric acid with the addition of a little hydrochloric acid. The sulphides remaining in the bottle are likewise dissolved in hot aqua regia, the solution washed into the dish, an excess of 50 per cent. sulphuric acid added, the solution evaporated, the residue taken up with water, the pale yellow separated sulphur filtered off, the filtrate saturated with excess of ammonia, a large quantity of ammonium sulphate (see above) added, and the nickel and cobalt then deposited electrolytically, using a cylinder, cone, dish, or crucible (*cf.* The Electrolytic Determination of Copper, p. 170). When from several decigrams up to 2 g. of nickel and cobalt are to be deposited, the solution is tested for complete deposition after six to twelve hours, according to the strength of current employed, by withdrawing 1 to 2 c.c. by means of a pipette, adding a few cubic centimetres of

[1] Fresenius and Bergmann's method, *Z. anal. Chem.*, 1879, **19**, 314; Fresenius, *Quantitative Analysis*, 7th ed., vol. ii., p. 304; W. J. Marsh, *J. Phys. Chem.*, 1914, **18**, 705.

sulphuretted hydrogen water, and warming in a test tube; if no yellow or brown coloration is produced the deposition is complete. It is to be specially noticed that the complete deposition by means of the current is considerably hindered by the presence of small quantities of nitrates or chlorides in the solution. The washing is carried out without breaking the current. The cathode is repeatedly washed with distilled water, finally with absolute alcohol, the dish or crucible dried on a boiling water bath, the cylinder or cone over a heated dish, and the cathode weighed after cooling for half an hour. Electrolytically deposited nickel is pure and possesses a yellowish gray colour; cobalt is of a darker gray colour, and, according to C. Winkler,[1] always contains some oxygen, up to 1·88 per cent. of the total amount of cobalt being deposited as hydrated cobaltic oxide. This does not appreciably influence the accuracy of the technical determination.

When nickel and cobalt are deposited quickly by electrolysis, using a current of from 1 to 1·5 ampères, the solution becomes very hot and much ammonia is lost; in order to prevent this, the crucible used as cathode, for example, is cooled by immersion in a dish partially filled with water.

The rapid electrolytic deposition of cobalt and nickel, using a rotating anode, is described by E. F. Smith.[2] Previous to the introduction of the electrolytic separation, nickel and cobalt were usually precipitated from the solution of the sulphides by excess of pure sodium hydroxide, heating, and then adding chlorine or bromine water. The precipitates of the hydrates of the sesquioxides were collected on an ash-free filter paper, persistently washed with hot water, dried, the filter paper ignited in a small platinum crucible exclusively used for the purpose, and then the oxides added and reduced by prolonged, strong ignition in a current of hydrogen. Since it is impossible to prevent some alkali being retained by the precipitate, the spongy metal must be extracted with hot water and then dried in an air bath.

The accurate determination of nickel and cobalt in substances rich in iron is especially tedious, since, even in very dilute solutions, the precipitate of basic ferric acetate (or sulphate) carries down with it considerable quantities of nickel and cobalt, and does not separate in a pure condition (*e.g.*, in the analysis of nickel steel) until after the fourth or fifth precipitation. This great inconvenience is completely overcome by the use of J. Rothe's ether method (p. 6). By this method, all the iron (excepting 1 to 2 mg.) goes into the ether, and nickel, manganese, aluminium, and practically all the cobalt into the aqueous hydrochloric acid solution. After running off the aqueous hydrochloric acid solution,

[1] *Z. anorg. Chem.*, 1894, **8**, 1, 291; *J. Chem. Soc. Abstr.*, 1895, **68**, 167.
[2] *Electro-Analysis*, pp. 126–133.

the ethereal ferric chloride solution in the top bulb is repeatedly shaken up with 10 c.c. of hydrochloric acid of sp. gr. 1·1, saturated with ether, and by this means all the cobalt is extracted in a short time. In order to remove the small amount of ferric chloride retained by the aqueous hydrochloric acid solution in the lower bulb, the solution is shaken up with 75 to 100 c.c. of ether. The solution obtained after treatment with ether is run into a shallow porcelain dish (15 cm. in diameter), an excess of 50 per cent. sulphuric acid added, gently warmed on the water bath (quarter of an hour) to drive off the dissolved ether, evaporated, the evaporation repeated with the addition of several cubic centimetres of water, the residue taken up with water, excess of ammonia and ammonium sulphate added, and the solution electrolysed as above.

If the substance contains much manganese, aluminium, and magnesium, as well as some zinc, it is well to precipitate the aluminium by boiling with sodium acetate; in the filtrate, to which some ammonium acetate and acetic acid are added, nickel and cobalt are precipitated as sulphides in a pressure bottle as described above. Any zinc sulphide precipitated with the nickel and cobalt is dissolved by treating the sulphides with hot, dilute hydrochloric acid, to which some sulphuretted hydrogen water is added; the pure sulphides of nickel and cobalt are then dissolved in aqua regia, the solution evaporated with excess of sulphuric acid, and finally electrolysed.

According to an old method, due to Mackintosh,[1] which is sufficiently accurate for technical purposes, the nickel and cobalt in substances either poor or rich in iron are determined by adding a slight excess of ammonia to the hydrochloric acid filtrate from the sulphuretted hydrogen precipitate, then adding a considerable quantity of ammonium sulphide, warming, and then digesting for some time with a large excess of 5 per cent. hydrochloric acid; the sulphides of iron, zinc, manganese, and traces of nickel and cobalt sulphides are dissolved, together with alumina. The residue (sulphides of nickel and cobalt with a little iron sulphide), after being washed with sulphuretted hydrogen water, slightly acidified with hydrochloric acid, is dissolved in aqua regia, the solution evaporated with sulphuric acid until fumes are evolved, the residue taken up with water, ammonia added, and nickel and cobalt deposited electrolytically.

In ores containing a high percentage of manganese, W. Witter[2] determines the nickel and cobalt as follows:—Iron and aluminium are precipitated as usual as basic acetates in the combined filtrates, and nickel, cobalt, and manganese by warming with sodium hydroxide and bromine water; the latter precipitate is then dissolved, and the solution

[1] *Chem. News*, 1887, **56**, 64.
[2] Private communication to Prof. Pufahl.

electrolysed. When most of the nickel and cobalt (after several hours) is deposited, the cone is washed, dried, and weighed. The solution is warmed in a beaker with the addition of hydrochloric acid until all the hydrated manganese dioxide has dissolved, ammonia and ammonium sulphide added, again warmed, acidified with 5 per cent. hydrochloric acid (which dissolves all the manganese sulphide), and filtered, etc., as above. By this means all the nickel and cobalt retained by the manganese dioxide is separated, which is not effected even by very prolonged electrolysis.

A rapid method[1] for separating nickel and cobalt from ferric iron, copper, zinc and arsenic consists of adding tartaric acid, then ammonia and finally potassium iodide. The nickel and cobalt are thrown down as the amines, $[Ni(NH_3)_6]I_2$; $[Co(NH_3)_6]I_2$.

B. SEPARATION OF NICKEL FROM COBALT[2]

1. QUANTITATIVE SEPARATION AND DETERMINATION OF COBALT

(a) By Potassium Nitrite.

The electrolytic deposit of the two metals is dissolved off the electrode in hot, dilute nitric acid (one volume of acid of sp. gr. 1·2 to three volumes of water), and the solution evaporated in a porcelain dish on the water bath. The residue is taken up in a few cubic centimetres of water, 5 g. of potassium nitrite added (in cold, saturated aqueous solution), and then acetic acid until oxides of nitrogen are evolved. The cobalt separates as brownish yellow potassium cobaltinitrite; the precipitation is complete after standing about twenty-four hours. The cobalt compound is then filtered off, washed with a cold, saturated solution of potassium sulphate, dissolved in hot, dilute sulphuric acid, the rose-red solution evaporated on the water bath, washed into a large platinum crucible, a large excess of ammonia added together with a considerable quantity of ammonium sulphate, the cobalt deposited electrolytically, and the nickel estimated by difference. If nickel and cobalt have been determined by the reduction of the sesquioxides in a platinum crucible, the spongy metals are shaken out, dissolved, etc., and the crucible again weighed; by strong ignition in hydrogen, some

[1] W. R. Schoeller and A. R. Powell, *Analyst*, 1917, **42**, 189, 388; 1919, **44**, 275.

[2] *Cf.* C. Krauss, *Z. anal. Chem.*, 1891, **30**, 227; *J. Chem. Soc. Abstr.*, 1891, **60**, 1139. This paper contains a summary and critical examination of methods for the separation and determination of cobalt and nickel.

nickel and cobalt alloys superficially with the platinum. This method is suited to all cases, especially when much cobalt is present together with a little nickel.

The filtrate from the potassium cobaltinitrite may be heated with excess of hydrochloric acid, diluted, made alkaline with sodium hydroxide, bromine water added, and the solution warmed so as to precipitate the nickel as the hydroxide, which is washed, dried, and reduced in hydrogen; or, the precipitate is dissolved in dilute sulphuric acid and aqueous sulphurous acid, evaporated, and the pure nickel deposited electrolytically.

(b) By Nitroso-β-Naphthol.[1]

Nitroso-β-naphthol forms compounds with nickel and cobalt, the cobalt compound, cobalti-nitroso-β-naphthol $[C_{10}H_6O(NO)]_3Co$, being insoluble in dilute hydrochloric acid. The solution of the two metals in dilute nitric acid is evaporated down with a slight excess of sulphuric acid, and the nitric acid completely driven off. The residue is dissolved in water, 5 c.c. of ordinary hydrochloric acid added, the solution warmed, and a freshly prepared hot solution of nitroso-β-naphthol in 50 per cent. acetic acid added until after the precipitate has subsided; a fresh addition of the solution produces no further precipitate. After digesting for several hours at a gentle heat, the very bulky precipitate of the cobalti-compound and much nitroso-β-naphthol is filtered off, washed first with cold, then with warm 12 per cent. hydrochloric acid, and finally with hot water. The filter is then folded together, placed in a weighed platinum crucible, the lid placed on, and the crucible heated with a large Bunsen burner. When no more combustible gases are evolved, the lid is removed, the crucible placed in a slanting position, and the difficultly combustible coke-like carbon completely burnt away; this requires from half an hour to an hour. If care be taken to give good access of air, the cobalt is left behind as tri-cobaltic tetroxide, Co_3O_4, of a black colour; reducing gases from the burner may cause considerable quantities of cobaltous oxide, and even of metallic cobalt to be formed, and there are some advantages in reducing the oxide with hydrogen and weighing as metallic Co. $Co_3O_4 \times 0{\cdot}7343 = Co$.

The method gives excellent results; on account of the bulkiness of the cobalti-compound, large quantities of cobalt are best precipitated according to the nitrite method.

[1] M. Ilinski and G. von Knorre.

[2] *Ber.*, 1885, **18**, 699; *J. Soc. Chem. Ind.*, 1885, **4**, 370; *Cf.* also *Chem. Zeit.*, 1895, **19**, 1421; *J. Soc. Chem. Ind.*, 1896, **15**, 51; Chapin, *J. Amer. Chem. Soc.*, 1907, **29**, 1929; Atack, *J. Soc. Chem. Ind.*, 1915, **34**, 641.

2. QUANTITATIVE SEPARATION AND DETERMINATION OF NICKEL

(a) By Dimethylglyoxime.

This method is described under "Nickel" in the section on "Iron and Steel," this volume, p. 66.

(b) By Dicyanodiamidine.

This method is also described under "Nickel" in the section on "Iron and Steel," this volume, p. 67.

(c) Volumetric Method.

There are various modifications of the volumetric method in which a potassium cyanide solution is used and silver nitrate and potassium iodide are added as an indicator. (See "Nickel" in the section of "Iron and Steel," this volume, p. 68.)

3. DETECTION OF COBALT

To the hydrochloric acid solution free from nitric acid, an equal volume of alcohol is added, the solution warmed, freshly prepared nitroso-β-naphthol solution added, and the solution boiled, when the purple-red cobalti-nitroso-β-naphthol separates; very small traces are precipitated only after standing for some time. Any brown nitroso-β-naphthol which separates may be dissolved by warming with 50 per cent. acetic acid.

F. W. Atack[1] has described an improvement of this method in which a solution of nitroso-β-naphthol in dilute sodium hydroxide is used, and J. Bellucci[2] finds that β-nitroso-α-naphthol when used as in Atack's method is far more sensitive than the α-β-naphthol more generally used, as it permits of the detection of 1 mg. of cobalt in 17 litres of water.

4. DETECTION OF NICKEL

According to L. Tschugaeff,[3] dimethylglyoxime is the most delicate reagent for the detection of nickel. It is added to the neutral or slightly ammoniacal solution, which is then boiled for a short time; a scarlet precipitate is formed, or, with only traces of nickel, a yellowish solution, from which the red precipitate separates on cooling. Distinct indications are obtained with solutions containing only 1 part of nickel

[1] *J. Soc. Chem. Ind.*, 1915, **34**, 641.
[2] *Gazz. Chim. Ital.*, 1919, **49**, 294.
[3] *Ber.*, 1905, **38**, 2520; *J. Soc. Chem. Ind.*, 1905, **24**, 941.

in 1,000,000 parts of water, and it is possible by its means to detect 1 part in 30,000,000.[1]

V. Fortini[2] detects nickel in alloys as follows: A polished surface of the alloy is prepared and lightly oxidised on the surface by means of an oxidising flame, the surface is cleaned with ether after which a solution of 0·5 g. of dimethylglyoxime in 5 c.c. alcohol to which is added 5 c.c. concentrated ammonia, is dropped on it.

This solution reacts quickly with nickel oxide and the red precipitate becomes visible before the solution has time to become appreciably darkened by copper.

C. Special Methods

1. Ores, etc.

Ores and Speisses containing Arsenic and Antimony are dissolved either by warming with nitric acid or with aqua regia, or (according to Hampe) in nitric and tartaric acids; the addition of tartaric acid is especially advisable if it is desired to carry out a complete analysis; Hampe takes 30 c.c. of ordinary nitric acid, and 10 g. of tartaric acid for 1 g. of speiss, etc. For the determination of copper, nickel, and cobalt, it is advisable first to roast the substance, then to dissolve it in aqua regia, boil the solution, heat the residue gently with hydrochloric acid, pass sulphuretted hydrogen in for a long time after diluting, and further treat the filtrate from the sulphuretted hydrogen precipitates as described above (p. 321). If the substance contains a high percentage of iron, the Rothe method (p. 6) is applied.

Pyrites containing Nickel, Magnetic Pyrites, and Nickel Mattes are likewise best roasted first, and the finely ground product dissolved in aqua regia, etc., as above.

Garnierite and similar Silicates are fused in a platinum crucible either with three to four times the weight of potassium sodium carbonate and some nitre, or with six times the weight of potassium hydrogen sulphate. The alkaline melt is lixiviated with water, evaporated to dryness with excess of hydrochloric acid, the silica rendered insoluble, the copper precipitated in the hydrochloric acid filtrate by means of sulphuretted hydrogen, and in the filtrate from the copper sulphide, aluminium, iron, manganese, calcium, and magnesium, separated as described above (p. 324). The melts obtained with potassium hydrogen sulphate and nitre are treated with water and hydrochloric acid, the silica filtered off, the copper precipitated in the filtrate with sulphuretted hydrogen, etc., as above. Very finely ground garnierite may also be decomposed by boiling with hydrochloric acid, aqua regia, or 50 per cent. sulphuric acid. The sulphuric acid or other solution to which

[1] A. Chaston Chapman, *J. Chem. Soc.*, 1917, **111**, 213.

[2] *Chem. Zeit.*, 1912, **36**, 1461. *J. Inst. Metals*, 1913, **9**, 238.

sulphuric acid is added is boiled until fumes of sulphuric acid begin to be evolved, the cool mass then treated with water, filtered, the copper precipitated from the filtrate, etc.

The sulphuric acid filtrate from the copper sulphide precipitate is finally boiled, with the addition of a few drops of bromine water, cooled, transferred to a beaker, a large excess of ammonia and some ammonium sulphate added and nickel and cobalt deposited electrolytically on a cone. The considerable quantities of earths and magnesia, as well as the manganese present, are without influence; if much iron is present, some may be deposited as metal, together with nickel and cobalt. The nitric acid solution of the nickel and cobalt is afterwards tested by saturating with ammonia, filtering off any ferric hydroxide which separates, which is weighed as ferric oxide, and the calculated quantity of iron deducted. $Fe_2O_3 \times 0.6994 = Fe$.

Nickel Copper Matte.—(*a*) One to two grams of the matte is dissolved in aqua regia, the solution boiled, the residue warmed with hydrochloric acid, water added, again boiled, and the copper precipitated as sulphide with sodium thiosulphate. The sulphur dioxide is expelled from the filtrate from the copper sulphide by boiling, the ferrous salt oxidised, the cooled solution neutralised with sodium hydroxide, sodium acetate added, etc., as described above. If the matte contains lead, the solution in aqua regia is evaporated with sulphuric acid, the residue taken up with water, the lead sulphate filtered off, the filtrate boiled, sodium thiosulphate added, etc., as above.

(*b*) One to two grams is roasted, the product dissolved in aqua regia, the solution evaporated down, the evaporation repeated with hydrochloric acid (20 to 40 c.c.), the concentrated solution extracted with ether by Rothe's method (*cf.* p. 6), the solution containing copper, nickel, cobalt, and manganese evaporated with sulphuric acid, and the copper deposited electrolytically; the solution, free from copper, is then evaporated to drive off the nitric acid, the residue dissolved in water, saturated with ammonia, and the nickel and cobalt deposited electrolytically. Any zinc present is precipitated with sulphuretted hydrogen, after neutralising the solution from the copper deposition with ammonia, making just acid with sulphuric acid, and diluting.

Slags (*e.g.*, from the refining of copper containing nickel, etc.) are decomposed with aqua regia, the solution evaporated, the filtrate from the silica treated with sulphuretted hydrogen, the sulphides filtered off, the sulphuretted hydrogen boiled off from the filtrate, which is then oxidised, neutralised with sodium hydroxide, and the iron and aluminium precipitated in the usual way. The nickel and cobalt in the filtrate are precipitated as the hydroxides with sodium hydroxide and bromine, the hydroxides dissolved, and the metals deposited electrolytically in presence of manganese.

Smalts.[1]—One gram of the fine powder is stirred up in a platinum dish with 5 c.c. of 50 per cent. sulphuric acid, about 20 c.c. of hydrofluoric acid added, gently warmed for one hour on the water bath, then evaporated, and heated on a sand-bath until sulphuric acid fumes are evolved. The cooled residue is taken up with water, any separated lead sulphate filtered off, and sulphuretted hydrogen passed into the filtrate, whereby copper, arsenic, and bismuth are precipitated. After boiling off the sulphuretted hydrogen from the filtrate, the iron is oxidised with nitric acid and subsequently precipitated together with the aluminium as basic acetate. Cobalt (nickel and manganese) is precipitated from the filtrate with sodium hydroxide and bromine water, or preferably potassium persulphate, the hydroxides washed, dissolved in dilute sulphuric acid[2] containing some sulphurous acid, and after evaporating, etc., the cobalt and nickel deposited electrolytically. The flocculent precipitate of hydrated manganese dioxide is collected on a filter paper, dried, the paper ignited, and the strongly ignited tri-manganic tetroxide weighed. Cobalt and nickel are dissolved from the cathode and separated by means of dimethylgloxime.

Sulphur is determined in ores, mattes, and speisses by Hampe's method (p. 192).

2. Commercial Nickel.

The metal comes on to the market as a fritted spongy mass, in the form of small cubes and round cylinders about 30 mm. high and 50 mm. diameter, and in a fused condition in the form of anode plates and granulated metal, and also as nodules from the Mond process.

In metal other than that from the Mond process, which is extremely pure, the impurities (iron, arsenic, sulphur, silicon, and carbon) usually amount to less than 1 per cent.; cobalt, to the extent of usually about 1 per cent. but frequently in considerably larger quantities, is always present, whilst manganese passes into the metal during the refining processes, and is hardly to be considered as an impurity. Fused nickel manufactured by the Fleitmann patents contains traces of magnesium (about 0·1 per cent.). Fused nickel may contain several per cent. of carbon and some silicon; the fritted metal may also contain carbon. By the reduction of nickel oxide by means of flour, etc., the latter introduces into cube nickel small quantities of lime, alumina, alkalis, and sand.

Nickel-copper containing up to 30 per cent. of copper, which cannot be distinguished by its colour from nickel, is prepared in some works for the manufacture of German silver, and comes on to the market in a granulated form.

[1] For the analysis of cobalt pigments, *cf.* pp. 524, 540.

[2] L. Dede, *Chem. Zeit.*, 1911, 35, 1077.

Analysis.—In sampling nickel cubes and cylinders of nickel, small pieces are chipped off by means of a sharp chisel; the granulated metal is used as such or the granules are divided by a chisel; borings of anode plates are used. Tin is detected by dissolving about 1 g. of the metal in nitric acid in a large test tube, diluting with water, and boiling; if tin is present, 5 g. of the metal is dissolved in a dish in 40 c.c. of nitric acid (sp. gr. 1·4), treated as in a bronze analysis (pp. 216 *et seq.*), the stannic oxide ignited in a platinum crucible, and, after weighing, treated with hydrofluoric acid and one drop of sulphuric acid to remove any admixed silica. The filtrate from the meta-stannic acid is evaporated with excess of sulphuric acid and treated as described below. If the metal dissolves to a nearly clear solution in nitric acid, 10 g. is weighed out, treated in a covered porcelain dish with 70 c.c. of nitric acid (sp. gr. 1·4), and 10 c.c. of water, warmed on the water bath until completely dissolved, 40 c.c. of 50 per cent. sulphuric acid added, the solution evaporated, and finally heated on a sand bath until fumes of sulphuric acid begin to be evolved. The cooled residue is dissolved by heating on a boiling water bath and stirring, and the silica (sand and some charcoal) filtered off. The filter paper containing the silica is ignited in a weighed platinum crucible, the weighed silica gently warmed for a long time with hydrofluoric acid and one drop of sulphuric acid (sand dissolves very slowly), the solution evaporated, the sulphuric acid driven off, and the residue, consisting at most of a little ferric oxide, ignited and weighed. If the metal contains much copper, this is deposited from the sulphate solution electrolytically, after the addition of nitric acid. If only a little copper is present, sulphuretted hydrogen is passed into the warmed sulphate solution for a long time and the copper thereby precipitated as sulphide, which is dissolved in nitric acid, the copper deposited electrolytically, and the electrolysis continued longer than necessary for the deposition of the copper, to see whether any arsenic is present. If only a few milligrams of copper is precipitated, the copper sulphide is roasted to oxide in a porcelain crucible, and weighed as such. If arsenic is found to be present, the sulphate solution, free from nitric acid, prepared from 10 or 20 g. of the metal, is brought into a flask, 5 to 10 g. of ferrous sulphate, together with much pure fuming hydrochloric acid, added, and the arsenic distilled off as chloride (*cf.* p. 205). The filtrate from the copper sulphide is evaporated to drive off the sulphuretted hydrogen, cooled, and made up to 500 c.c. in a graduated flask. The nickel and cobalt from 100 c.c. of this solution (corresponding to 2 g.) are deposited electrolytically (p. 322), both metals weighed, the cobalt determined as tri-cobaltic tetroxide by Ilinski and von Knorre's method (p. 326), the solution from the nickel and cobalt filtered, and any magnesium present precipitated by the addition of a few drops of aqueous phosphoric acid. For the determina-

tion of the iron and manganese, the remaining 400 c.c. (corresponding to 8 g. of metal) is diluted to 1 litre, the solution oxidised with bromine and the iron and manganese precipitated by boiling with ammonia in excess. The precipitate is collected on an iron-free filter paper, washed for a short time, then dissolved in hot, dilute hydrochloric acid, after which the solution is again oxidised and precipitated with ammonia, filtered, the precipitate washed, dried, strongly ignited in a weighed porcelain crucible with good access of air, and the mixture of oxides of iron and manganese weighed. The oxides are then dissolved in hydrochloric acid, the solution evaporated on the water bath, and the residue taken up with a few drops of hydrochloric acid and water. The ferric chloride thus obtained may be titrated with stannous chloride, or the solution may be evaporated with sulphuric acid, diluted with water, reduced with zinc, and the ferrous sulphate titrated with potassium permanganate (*cf.* pp. 22 *et seq.*). The ferric oxide thus found is deducted from the weight of mixed oxides, and the difference is tri-manganic tetroxide. If much iron and manganese are present, they are separated by the sodium acetate method, the manganese precipitated in the filtrate as dioxide, the iron precipitate again dissolved in hydrochloric acid, precipitated with ammonia, and finally weighed as ferric oxide. The manganese is weighed as tri-manganic tetroxide.

L. Bertiaux[1] dissolves the metallic nickel in a mixture of hydrochloric and sulphuric acids, adds an excess of ammonia and deposits nickel, cobalt and copper together electrolytically. The deposit is then dissolved in nitric acid and the copper determined electrolytically, the cobalt as cobaltinitrite and the nickel electrolytically. Iron, manganese, aluminium, calcium and magnesium are determined in the liquid from the first deposit. Silica and sulphur are determined in a separate quantity, arsenic and antimony by distillation (p. 207) and carbon by combustion as described below.

Determination of Sulphur.—Ten grams is dissolved in pure nitric acid, the excess of acid evaporated off, twice evaporated to dryness with about 100 c.c. of pure hydrochloric acid, the residue taken up with hydrochloric acid and water, diluted to about 300 c.c., and the sulphur precipitated with barium chloride.

Determination of Carbon.—The carbon (together with the sand) remaining after dissolving 10 g. of nickel cubes in nitric acid is collected on an asbestos filter, washed, the filter transferred to a porcelain boat, dried, the carbon burnt in a porcelain tube, and the carbon dioxide absorbed in potash bulbs. $CO_2 \times \frac{3}{11} = C$.

Fused nickel (anode plates, granules) may contain several per cent of carbon. Three grams of the finest possible drillings or granules are warmed in a beaker on a boiling water bath with a concentrated

[1] *Ann. Chim. anal.*, 1912, 18, 377.

solution of copper ammonium chloride (150 g. $NH_4Cl.CuCl_2 \cdot 2H_2O$ per 500 c.c.) for twenty-four to forty-eight hours, or until the nickel is completely dissolved, and the residue collected on an asbestos filter and washed, etc., as above. The determination of the small quantities of aluminium, calcium, and alkalis which occur in nickel cubes offers no difficulties, but is very lengthy, and is, therefore, not carried out in commercial analyses.

Determination of Magnesium.[1]—Fifteen to twenty g. of the metal is dissolved in nitric acid, and the solution evaporated twice to dryness to dehydrate the silica. The residue dissolved in hydrochloric acid is treated with ammonium chloride, bromine water and ammonia to separate iron, etc., the filtrate from this precipitate is neutralised with hydrochloric acid and potassium cyanide added until the precipitate of nickel cyanide just redissolves. Twenty c.c. of a 10 per cent. solution of sodium hydrogen phosphate, together with one third of the bulk of solution as ammonia, are added and the whole allowed to stand overnight. The precipitate is filtered, washed with dilute ammonia, dissolved, reprecipitated, and finally ignited and weighed as $Mg_2P_2O_7$.

3. Metallic Cobalt.

The metal comes into commerce as cubes, and contains only very small quantities of impurities (nickel, iron, copper, carbon, sand); it is used for electro-plating and in the manufacture of certain alloys; when necessary, its analysis is conducted in a similar manner to that described for nickel, the nickel being separated from the solution containing cobalt and nickel by means of dimethylgloxime.

4. Nickel Alloys.

The alloys to be considered are chiefly those with copper, such as coinage alloys, containing 75 per cent. of copper, and 25 per cent. of nickel, alloys for bullet envelopes, containing about 80 per cent. of copper and 20 per cent. of nickel, and those with copper and zinc, such as nickel, silver, argentan, nickelin, etc.

Other alloys of importance are Monel metal, an alloy obtained by the direct smelting of certain ores, and containing 60 to 72 per cent. of nickel, 0·5 to 6·5 per cent. of iron and 1 per cent. of manganese; and ilium, a complex alloy containing 60 per cent. of nickel, 21 per cent. of chromium, 6 per cent. of copper, together with small quantities of molybdenum, tungsten, iron, aluminium, manganese and silicon. There are also alloys especially used for winding of electric resistance furnaces, such as nichrome, containing 11 to 25 per cent. of chromium, and usually iron (up to 25 per cent.); platinoid, containing 60 per cent. of copper,

[1] K. Chalupny and K. Breisch, *Chem. Zeit.*, 1922, 46, 91; *J. Inst. Metals*, 1922, **28**, 684.

24 per cent. of zinc, 14 per cent. of nickel and 1 to 2 per cent. of tungsten; rheostan, containing 52 per cent. of copper, 18 per cent. of zinc, 25 per cent. of nickel and 5 per cent. of iron; and manganin, containing 4 to 40 per cent. of nickel, 60 to 80 per cent. of copper and 1 to 12 per cent. of manganese.

Analysis.—One gram of drillings is dissolved in 10 to 15 c.c. of nitric acid (sp. gr. 1·2) in a covered porcelain dish on the water bath, the solution evaporated with 5 c.c. of 50 per cent. sulphuric acid, any lead sulphate (from the spelter) which separates filtered off, and the copper in the filtrate deposited electrolytically in a crucible or dish, after the addition of nitric acid. If it is desired to precipitate the copper as sulphide by means of sulphuretted hydrogen, the filtrate from the lead sulphate is diluted to about 300 c.c. and 30 to 50 c.c. of hydrochloric acid (sp. gr. 1·124) added to prevent the precipitation of zinc. If this addition is not made, the copper sulphide precipitate is first washed with hydrochloric acid to which some sulphuretted hydrogen water is added, and then with very dilute sulphuretted hydrogen water acidified with one drop of sulphuric acid. The filtrate is evaporated, the residual sulphate solution somewhat diluted, nearly neutralised with ammonia, diluted to 400 to 500 c.c., and sulphuretted hydrogen passed in for a considerable time (one to two hours) to precipitate the zinc as sulphide. The solution from the deposited copper is evaporated till the sulphuric acid begins to fume in order to remove the nitric acid; the cooled residue is taken up with 100 c.c. of water, the solution neutralised in presence of a strip of Congo red paper until it gives just a faint acid reaction, then largely diluted and the zinc precipitated with sulphuretted hydrogen (*cf.* pp. 293 *et seq.*). The zinc sulphide is filtered off after twelve hours, and washed with dilute sulphuretted hydrogen water containing several grams of ammonium sulphate. The filtrate, after the addition of 5 c.c. of sulphuric acid to prevent separation of nickel sulphide is evaporated in a porcelain dish to about 100 c.c., the cooled solution washed into a 200 c.c. beaker, 50 c.c. of strong ammonia added, the solution then cooled, and the nickel and cobalt deposited electrolytically on a conical cathode. The iron and manganese are filtered off from the solution after electrolysis, and separated and determined as described under the analysis of nickel (pp. 332 *et seq.*). Any hydrated manganese dioxide which adheres to the anode is removed by a glass rod, the end of which is covered with a piece of rubber tubing. A separation of nickel and cobalt is not necessary.

German silver and similar alloys frequently contain some tin (added to improve the colour of the metal), which is recognised on dissolving the alloy in nitric acid, diluting the solution, and boiling. It is determined as in the analysis of bronze (p. 216). Copper-nickel

alloys, for parts of machinery, not infrequently contain several per cent. of aluminium; in the analysis, the copper is first separated electrolytically, the nitric acid removed from the remaining solution, excess of ammonia then added, and the nickel also deposited by electrolysis. The cloudy solution containing the aluminium hydroxide is then neutralised with acetic acid, diluted, boiled, the precipitate filtered off, washed, ignited, and the ferric oxide containing alumina weighed. The mixed oxides are fused in a platinum crucible with six times their weight of potassium hydrogen sulphate, the melt dissolved in hot, dilute sulphuric acid, the ferric sulphate reduced with zinc, and the iron titrated with potassium permanganate.

Nichrome[1] and similar alloys are somewhat difficult to dissolve; a suitable quantity is decomposed with aqua regia and evaporated to dryness. The residue is treated with hydrofluoric acid for the removal of silica, taken up with acid, and any insoluble material remaining is fused with sodium peroxide, and the fused mass dissolved in the usual manner. Nickel is determined by the potassium cyanide method (p. 68); the iron, after separation from chromium, is reduced by means of zinc and titrated with potassium permanganate. Chromium is determined by the addition of manganese sulphate, reduction by ferrous ammonium sulphate and titration of the excess iron with permanganate or bichromate. Manganese is determined in a separate portion of the solution by precipitating with potassium chlorate, solution of the precipitated manganese in ferrous ammonium sulphate and subsequent titration with permanganate. Zinc is determined in the filtrate from the iron-chromium precipitate by the potassium ferrocyanide method.

Silver-plated Nickel Silver.—For the determination of the coating of silver, the well-cleaned articles (spoons, forks, etc.) are suspended by means of iron or platinum wires, connected to the positive pole of a battery, in a glass vessel filled with a 2 to 3 per cent. solution of potassium cyanide, and the silver deposited electrolytically on to a strip of thin copper foil, which serves as the cathode. The desilvered articles are removed from the bath, excess of hydrochloric acid added to the solution (under a good fume cupboard on account of the evolution of hydrocyanic acid) and the solution evaporated so as to separate the silver as chloride; the copper foil, with the deposited silver, is dissolved in nitric acid, and the silver precipitated from the diluted solution with a slight excess of hydrochloric acid.

The removal of the layer of silver by means of nitric acid is not possible, since silver from the solution is always re-deposited on the alloy. The scraping off of the silver with suitable instruments is very tedious and gives low results, since the "amalgamation" which

[1] E. W. Reid, *Ind. Eng. Chem.*, 1917, 9, 488.

precedes the silvering of nickel silvers rich in nickel eats somewhat deeper into the alloy than the electrolytically deposited silver. If the articles to be analysed may be destroyed, they can be completely dissolved in nitric acid, etc., or melted up in a crucible in a coke wind-furnace, an ingot cast and weighed, a weighed quantity of drillings from the ingot dissolved in nitric acid, and the silver determined in the resulting solution.

5. Cobalt Alloys.

Stellite is an alloy containing cobalt, chromium, tungsten and carbon; it possesses remarkable cutting properties, and is used in the manufacture of special tools. In some varieties of stellite, molybdenum is used in place of tungsten. A modified alloy of the same class known as Festel metal contains cobalt, iron and chromium. A cobalt alloy with chromium, analogous to nichrome, is sometimes used for winding electric furnaces.

Analysis.—A small quantity of the alloy is decomposed with aqua regia, the solution diluted, tungstic acid filtered off, and the treatment continued for cobalt and chromium.

When molybdenum is present instead of tungsten the method described by J. R. Camp and J. W. Marden[1] is followed. A small quantity is taken into solution with aqua regia, and when solution is complete 3 c.c. concentrated sulphuric acid is added, after which the solution is evaporated until white fumes appear. The solution is diluted, transferred to a pressure flask, gassed with sulphuretted hydrogen, and the flask securely corked and placed in boiling water where it is left for one hour. The molybdenum sulphide is filtered off, washed, ignited to MoO_3 and weighed. The solution is boiled until free from sulphuretted hydrogen, and the cobalt is precipitated by adding sodium peroxide. The precipitated cobalt hydrate is washed, dissolved in hydrochloric acid, reprecipitated with sodium peroxide, filtered, washed and ignited to Co_3O_4. The filtrate is acidified with sulphuric acid, and the chromium present determined by reducing with ferrous ammonium sulphate and titrating the excess with bichromate solution.

6. Determination of the Nickel on Nickel-plated Iron Articles.

The coating of nickel is dissolved off with hot, dilute nitric acid (one volume of acid of sp. gr. 1·2 to one volume of water), and the nickel is determined in the solution by the dimethylglyoxime method (p. 66).

[1] *Ind. Eng. Chem.*, 1920, **12**, 998.

MANGANESE

Of the numerous manganese ores, only the oxides are of technical importance, and of these more especially, *Pyrolusite*, MnO_2, and *Psilomelane*, according to Rammelsburg, $RO.4MnO_2$ (in which R = Mn, Ba and K_2), which usually contain in addition some silica and small quantities of copper, cobalt, magnesium, and calcium. About nine-tenths of all the manganese ores and ores containing manganese are used for the manufacture of iron-manganese alloys such as spiegeleisen and ferro-manganese, whilst the remainder is used for the manufacture of chlorine, bleach, manganates and permanganates, glass, the preparation of varnishes, etc., and to a small extent for the production of manganese-copper alloys.

The methods for the determination of manganese in manganese ores and iron ores containing manganese are fully described in the section on Iron and Steel (pp. 7 and 29). The most frequently used gravimetric method of determination is the peroxide method. Of the volumetric methods, that of Volhard (p. 29) and the bismuthate method (p. 56) are the most generally used.

For the analysis of iron-manganese alloys, *cf.* Iron, p. 52. The analysis of manganese-copper alloys is described on p. 215 (Manganese Copper) and p. 216 (Manganese Bronze). The analytical methods for pyrolusite are described in Vol. I., pp. 576 *et seq.*

CHROMIUM

Chromite or *Chrome iron ore* (approximating to the formula $Cr_2O_3.FeO$), which occurs in large quantities, is the material from which all chromium compounds and chromium iron alloys are prepared. The mineral itself always contains more or less ferric oxide, alumina, and magnesia; the content of chromic oxide in the ore as it comes on to the market, varies between 30 and 62 per cent.

Detection of Chromium.—By fusing up the substance mixed with sodium carbonate in a small platinum spoon, or on a piece of foil or platinum wire, to a high temperature, and with good access of air, a yellow melt consisting of a chromate is produced, which, when dissolved in water, produces a yellow precipitate of lead chromate after acidifying with acetic acid and addition of lead acetate solution. Very minute

quantities of chromium are recognised in iron and steel during the determination of the manganese by Hampe's chlorate method (p. 53), the presence of chromium producing a yellow coloration in the filtrate from the manganese dioxide.

The ore is usually analysed by fusing a small quantity (0·35 to 0·5 g.) of the very finely ground substance with oxidising and fluxing agents, lixiviating the fusion with water, and titrating the chromic acid in the solution. In the older methods of fusion some of the ore remained unattacked, and this had to be fused up again, which rendered the determination very tedious. This difficulty is entirely removed by the use of sodium peroxide, either alone or mixed with sodium hydroxide. The fusion methods of J. Spüller, S. Kalman, and of J. Lambert, described in the section on Iron, p. 12, are applicable to all substances containing chromic oxide or chromium; the chromic acid in the solution, after the excess of sodium peroxide is removed, is titrated by the method given on p. 72.

J. Rothe[1] fuses 0·5 g. of the very finely powdered ore in a platinum crucible with four times the weight of a mixture of equal parts of nitre and previously dehydrated sodium hydroxide, heats to a dull red heat, and thus obtains complete decomposition of the substance.

The chromic acid in all soluble chromates is titrated by Schwarz's method, by acidifying with sulphuric acid, adding a weighed excess of ferrous ammonium sulphate, and titrating back the excess with potassium permanganate. Schwarz treats lead chromate by intimately rubbing it up with excess of ferrous ammonium sulphate and hydrochloric acid, adding a large quantity of water and titrating the solution with permanganate.[2]

L. Duparc and A. Leuba have worked out the following method for the analysis of chrome iron ores[3]:—They discard the fusion with sodium peroxide, since crucibles of silver, platinum, or copper are thereby strongly attacked, as well as the fusion with acid potassium sulphate, which does not work well and is never quantitative, and substitute sodium carbonate in the following manner, which must be carried out accurately in every detail:—The mineral is ground exceptionally finely in an agate mortar, "bagged" through silk gauze, dried, not more than 0·2 to 0·3 g. mixed with 5 to 6 g. of pure sodium carbonate and heated for eight hours in a platinum crucible closed with the lid. Finally, the heat is increased and the crucible lid left half open. When the fusion is completed, the crucible is dipped into a porcelain dish containing 100 c.c. of cold water, in which it is allowed to remain for several hours.

[1] Private communication to Prof. Pufahl.

[2] For analysis of chrome pigments see pp. 483, 511, 541.

[3] *Chem. Zeit.*, 1904, **28**, 518; *J. Chem. Soc. Abstr.*, 1904, **86**, 592; and private communication to Prof. Pufahl.

The contents of the crucible, washed out with water, are warmed on a water bath with hydrochloric acid, so as to dissolve the suspended oxide of iron completely, the solution evaporated to dryness, again moistened with hydrochloric acid and again evaporated, this being repeated three times so as to separate the silica. The residue is finally taken up with dilute hydrochloric acid, the silica filtered off and determined in the usual way. Ammonia is added in slight excess to the filtrate, and the solution warmed on the water bath until the smell of ammonia is no longer recognisable. The precipitate contains the hydroxides of chromium, iron, and aluminium; it is filtered off, washed, dried, ignited in a platinum crucible, and the mixture of the three oxides weighed. Calcium and magnesium are determined in the filtrate by the usual methods. For the separation of the three oxides, the mixture is very finely ground, a portion weighed out, and again fused in a platinum crucible with sodium carbonate. On extraction with water, the iron remains as insoluble oxide, the chromium is dissolved quantitatively as sodium chromate and the aluminium as sodium aluminate. The solution is carefully neutralised with nitric acid, care being taken to avoid any excess of this acid, a slight excess of ammonia added, the excess driven off, the precipitated hydroxides dissolved in hydrochloric acid, the precipitation and solution repeated, the precipitate filtered off, washed (first with water containing sodium carbonate, then with pure water), and ignited, when perfectly pure white alumina is finally obtained. The chromate in the filtrate is reduced to chloride, and the chromium hydroxide precipitated with ammonia. If the slightest excess of nitric acid is used for the neutralisation of the solution, it reacts with the sodium chromate, to form a green hydroxide of aluminium containing chromium, which is precipitated on the addition of ammonia. Acetic acid reacts in a similar manner. Hydrochloric acid cannot be used on account of its reducing action on the chromate.

TUNGSTEN

The following are the most important minerals from which tungsten and its compounds are obtained: *Wolframite*, consisting of isomorphous mixtures of $MnWO_4$ and $FeWO_4$, containing 76 per cent. of tungstic oxide and 5 to 7 per cent. of manganese; *Hübnerite*, a similar mineral but containing generally about 16 per cent. of manganese; *Scheelite*, $CaWO_4$, containing 80·5 per cent. of tungstic oxide and *Ferberite* ($FeWO_4$), which may contain traces of manganese. Less important ores are *Tungstite*, or *Wolframine* (WO_3), *Stolzite* ($PbWO_4$), and *Cuproscheelite* ($CuCa_2(WO_4)_3$).

For the determination of the contained tungstic acid, the very finely ground ore is decomposed by continued boiling with hydrochloric acid, followed by aqua regia or nitric acid, hydrochloric acid with potassium chlorate, equal parts of hydrochloric and hydrofluoric acids or a solution of sodium or potassium hydroxide, or it is fused in a platinum crucible with potassium sodium carbonate if it contains no arsenic (arsenical pyrites, etc.), sodium peroxide, potassium bisulphate, etc.

Methods of Analysis

1. Scheele's Method.[1]

One to two grams of the very finely powdered mineral (wolframite or scheelite), dried at 100°, is repeatedly evaporated to dryness in a porcelain dish with an excess of hydrochloric acid, to which some nitric acid is finally added, and the residue is heated each time to about 95°. The final residue is then digested with hydrochloric acid and water, the tungstic acid, which is invariably contaminated with silica, filtered off, washed with hot water, washed off the filter paper into a beaker, dissolved in warm, dilute ammonia, the solution filtered through the same filter paper into a weighed platinum dish, the siliceous residue heated with hydrofluoric acid and a few drops of sulphuric acid, the solution of ammonium tungstate evaporated, the residue completely dried, and finally converted by strong ignition into yellow tungstic oxide. $WO_3 \times 0{\cdot}7931$ = Tungsten.

Wolframite containing tin-stone or arsenical pyrites is best treated according to this method. For the determination of the tin in tungstic

[1] *Cf.* Ledoux & Co., *South Dakota School of Mines Bull.*, 1918, **12**, 151.

acid containing stannic acid, J. H. Talbot[1] fuses the mixed oxides with six times their weight of potassium cyanide in a porcelain crucible for half an hour, dissolves the fusion in hot water, collects and weighs the metallic tin, and deducts the corresponding weight of stannic oxide from the weight of the impure tungstic oxide.

2. Berzelius' Method.

One gram of the ore is fused in a nickel crucible with three to four times the weight of potassium sodium carbonate (the absence of arsenic and antimony is assumed), the cold melt extracted with hot water, the solution neutralised with nitric acid, the carbon dioxide expelled by warming, iron and alumina precipitated by means of ammonia, the solution again neutralised with nitric acid, then a cold saturated solution of mercurous nitrate containing precipitated oxide of mercury in suspension[2] added until no further precipitate is formed, and finally a few drops of ammonia added until the precipitate begins to turn brown. The precipitate is allowed to settle, filtered off, washed with water to which some of the mercurous nitrate solution is added, dried, and converted into tungstic oxide by careful ignition in an open platinum crucible in the fume cupboard. By evaporating the residue with a few c.c. of hydrofluoric acid and one drop of sulphuric acid, any silica carried down with the tungstic acid may be removed. The tungstic acid may be purified by solution in ammonia and evaporation to dryness as in method 1.

3. Bullnheimer's Method.

This method[3] takes into special consideration the numerous minerals (scheelite, stolzite, tin-stone, arsenical pyrites, molybdenite, fluor-spar, bismuth, copper pyrites, quartz, mica, and other silicates) which accompany wolframite both in poor and in rich ores.

The determination of the tungsten is carried out as follows:—One to two grams of finely powdered ore is mixed in a nickel crucible with 4 g. of sodium peroxide, a small piece of sodium hydroxide (about 3 g.) placed in the mixture so that it rests on the bottom of the crucible, and then the crucible warmed over quite a small Bunsen flame until the contents appear quite moist. The addition of sodium hydroxide serves to render the melt fluid, thereby making it easier to prevent portions of the ore settling and adhering to the bottom of the crucible. If this

[1] *Am. J. Sci.*, 1870 (ii), 50, 246. *Cf.* B. Setlik, *Chem. Zeit.*, 1889, 13, 1479.
[2] *Cf.* L. Gugliolmelli and U. Hordh, *Chem. Abs.*, 1918, 12, 794.
[3] *Chem. Zeit.*, 1900, 24, 870; *J. Chem. Soc. Abstr.*, 1901, 80, 41.

occurs, the crucible soon becomes eaten into, whilst otherwise it can be used twenty times. The crucible is then heated with a larger flame, continually stirring with a nickel spatula, until the whole is quite liquid and the bottom of the crucible begins to glow. Wolframite is thus completely decomposed, whilst tin-stone is only partially attacked, and some is left behind unchanged. After the fusion has solidified, the crucible and contents, whilst still hot, are placed in a beaker containing water; when the contents have dissolved, the crucible is removed and the solution washed into a 250 c.c. flask. If the solution is coloured green with manganate, hydrogen peroxide is added till decolorised. After cooling, the flask is filled up to the mark, half the solution filtered through a dry, folded paper, and 20 g. of ammonium nitrate added. When the latter is dissolved, the solution is allowed to stand quietly until the silica and stannic acid have settled, and then a sufficient quantity of magnesium nitrate solution is added, in small quantities at a time, with continual stirring, to precipitate any arsenic or phosphoric acids present.

The ammonium and magnesium salts used must be the nitrates, since chlorides or sulphates interfere with the subsequent precipitation with mercurous nitrate. After standing for from six to twelve hours, the precipitate is filtered off and washed, first with ammonia and then with water. It is essential to allow the silica and stannic oxide to settle before adding the magnesium nitrate, otherwise the precipitate easily carries some tungsten down with it. The ammoniacal solution is then made slightly acid with nitric acid, and after cooling, 20 to 30 c.c. of mercurous nitrate solution added. (The mercurous nitrate solution is prepared from 200 g. of mercurous nitrate, 20 c.c. of concentrated nitric acid, a little water, then warmed, and when dissolved, diluted to 1000 c.c. and kept over mercury.) After several hours, ammonia is added until the solution has only a slight acid reaction; it is then allowed to stand until the liquid over the dark precipitate has cleared. The precipitate is then filtered off and thoroughly washed with water containing mercurous nitrate. By the foregoing procedure, the precipitate will be found to be retained completely by the filter paper, and the washings will be perfectly clear. After drying, the filter paper is ignited, heated under the fume cupboard over a Bunsen burner, and then more strongly over a blow-pipe with access of air until of constant weight. If much molybdenum is present, which is seldom the case, its volatilisation is complete only after a considerable time. The same end is somewhat more quickly attained, if, after the first strong ignition, some ammonium chloride is mixed with the contents of the crucible, which are then strongly ignited, first with the lid on and finally with the lid off.

4. Cremer's Method.[1]

The finely divided ore is fused with potassium persulphate and the cooled mass extracted with hydrochloric acid and water and filtered. To the hot filtrate an excess of a solution of cinchonine in hydrochloric acid (1 : 1) is added, the whole is boiled, allowed to stand overnight, then filtered and the precipitate washed with dilute cinchonine solution, dried, ignited, and weighed as WO_3. This is dissolved in ammonia, filtered and any residue ignited, weighed, and deducted from the weight of the WO_3.

5. Analysis of low-grade Wolfram Ores.

Hutchin and Tonks[2] have worked out the following method, which is specially suitable for the determination of tungstic acid in low-grade wolfram ores, but it is not suitable for scheelite. About 5 g. or more, according to the richness of the sample, is weighed and digested in a porcelain dish with 20 c.c. of a 25 per cent. solution of sodium hydroxide (free from chloride) on a water bath for thirty to forty-five minutes. After dilution, a little sodium peroxide is added to oxidise any decomposition products of sulphides and the solution diluted to 250 c.c. in a graduated flask; 200 c.c. is filtered through a dry filter paper, acidified with nitric acid, and then made alkaline with ammonia. The solution is then boiled, filtered, the precipitate washed, the filtrate made slightly acid with dilute nitric acid, and mercurous nitrate added in excess, followed by a few drops of dilute ammonia. On stirring and warming, the precipitate settles readily; it is filtered off, washed with a dilute solution of mercurous nitrate, the paper and precipitate ignited together in a porcelain crucible, or, if the ore is free from arsenic, in a platinum crucible, and weighed as tungstic oxide.[3]

6. Analysis of Metallic Tungsten.[4]

Metallic tungsten, if in fine powder, is dissolved in ammonia containing hydrogen peroxide or in a solution of ammonium persulphate. Coarser powders are alternately moistened with nitric acid and ignited in air and the ignited tungstic trioxide is dissolved after very fine grinding by adding it slowly to hot concentrated ammonia. Massive metallic tungsten is dissolved electrolytically in ammonia containing ammonium persulphate, using 1 to 2 amp. at 2·5 to 3·5 volts, or by dropping into nearly fused alkali nitrate.

[1] *Eng. and Min. J.*, 1895, **59**, 345; *cf.* H. W. Hutchin, *Trans. Inst. Min. and Met.*, 1918, **27**, 354.

[2] *Trans. Inst. Min. and Met.*, 1908-9, **18**, 425; *cf.* L. Weiss and A. Martin, *Z. anorg. Chem.*, 1910, **65**, 287.

[3] *Cf.* also Foote and Ransom, *Eng. and Min. J.*, 1918, **105**, 836.

[4] H. Arnold, *Z. anorg. Chem.*, 1914, **88**, 74, 333: *J. Inst. Metals*, 1914, **12**, 330; 1915, **13**, 351.

The alkaline solution obtained is mixed with tartaric acid (one molecule for each molecule of tungstic oxide), acidified with hydrochloric acid and saturated hot with sulphuretted hydrogen. The precipitate obtained is free from tungsten but contains any molybdenum that may be present and is examined by the usual methods for copper, lead, bismuth, arsenic, antimony and tin. The tungsten is then precipitated from the filtrate by pouring it slowly into an excess of hot strong hydrochloric acid. The precipitate is filtered and well washed with dilute acid, after which the remaining metals are determined in the filtrate by the usual methods.

Carbon in tungsten powder is determined by combustion in oxygen and absorption of the carbon dioxide in potash. For massive tungsten electrolytic solution with low current density must be used, the anode residue being submitted to wet combustion with chromic acid (see pp. 41 *et seq.*).

Sulphur in tungsten powder is best determined by combustion in oxygen and absorption of the sulphur dioxide in sodium hydroxide and bromine. For massive tungsten a solution is first prepared and sulphur precipitated from the concentrated solution, in the presence of nitric and oxalic acids by means of barium chloride.

Silicon is mainly present as oxide and is determined by volatilisation with hydrofluoric acid, after the conversion of the metal into tungstic trioxide. A deep platinum crucible should be used to avoid loss of tungsten as fine dust. An alternative method for silicon consists in mixing an alkaline solution of the metal with tartaric acid and acidifying with formic or oxalic acid. The solution is evaporated to dryness, dried at 120° and digested with hot water until all the tungsten is dissolved and silica remains, which is filtered off, ignited, and weighed.

Arsenic is precipitated from an alkaline solution of the tungsten by means of magnesia mixture. As the precipitate is always contaminated with tungsten it is distilled with hydrochloric acid and cuprous chloride and the arsenic collected and titrated with iodine. Phosphorus is determined by precipitation with magnesia mixture, evaporating the precipitate obtained with hydrobromic acid to remove arsenic and then reprecipitating the phosphorus.

URANIUM

Uranium compounds (sodium and ammonium uranate) and uranyl nitrate, which are used in the manufacture of glass and for painting on porcelain, are for the greater part prepared from *Uranium pitchblende* (uranous-uranic oxide, U_3O_8), containing up to 80 per cent. intimately mixed with pyrites, arsenical pyrites, galena, etc., and which is found in Cornwall, at Joachimsthal, Johanngeorgenstadt, Adrianople, and other localities, *Carnotite*, $K_2O . 2UO_3 . V_2O_5 . 3H_2O$, found in Colorado and Utah, and to a lesser extent from naturally occurring hydrated copper uranium and calcium uranium phosphates, such as tobernite and autunite.

Poorer ores which come into commerce contain 30 to 60 per cent. of U_3O_8; the *Uranium sands* of Carolina, Connecticut, and Colorado contain only from 8 to 18 per cent. Uranium minerals always contain radium and helium.[1] Small amounts of compounds of copper, bismuth, silver, zinc, arsenic, and aluminium are also often present.

METHODS OF ANALYSIS[2]

1. H. Rose's Method.

About 1 g. of finely ground substance, dried at 100°, is warmed in a flask with 100 c.c. of strong nitric acid, the solution evaporated to dryness, the evaporation repeated with 20 c.c. of hydrochloric acid, the residue taken up with hydrochloric acid, 50 c.c. of a saturated aqueous solution of sulphur dioxide added, the solution warmed to reduce the arsenic oxide, boiled, and sulphuretted hydrogen passed in for some time after further dilution. The precipitate is filtered off, an excess of a cold, saturated solution of ammonium carbonate added to the filtrate, and then ammonium sulphide; zinc, iron, manganese, nickel, and cobalt separate as sulphides, whilst all the uranium remains in solution as uranous carbonate. When the precipitate of sulphides has settled, the supernatant liquid is poured through a filter paper, the precipitate repeatedly washed by decantation with water containing some ammonium sulphide and ammonium carbonate, after which the precipitate is brought on to the paper and thoroughly washed. The filtrate is boiled for some time, hydrochloric acid added to decompose the ammonium sulphide, again boiled for a quarter of an hour, and then the uranous oxide oxidised by boiling with a little nitric acid. All the uranium is now precipitated as hydroxide with a slight excess

[1] *Cf.* C. Baskerville, *Eng. and Min. J.*, 1909, **87**, 257.

[2] A summary of the best methods of analysis is given by Kern, *J. Amer. Chem. Soc.*, 1901, **23**, 685.

of ammonia, the precipitate washed with dilute ammonium chloride solution, dried, and, by igniting in a platinum crucible with good access of air, converted into the oxide U_3O_8 ($UO_2 . 2UO_3$), which is weighed. $U_3O_8 \times 0{\cdot}8481$ = Uranium. The oxide is dissolved in hydrochloric acid, the solution diluted and any insoluble residue filtered off, ignited, weighed, and the weight deducted from the original weight. The amount of uranium in the ore is usually expressed as a percentage of U_3O_8.

2. A. Patera's Technical Assay.

One to five grams of the finely powdered ore is dissolved by heating for some time with a slight excess of nitric acid (sp. gr. 1·2), the solution diluted, ferric chloride added if necessary, then excess of sodium carbonate solution, boiled for a short time, the precipitate filtered off and washed with hot water. The filtrate contains all the uranium and only traces of other metals. It is neutralised with hydrochloric acid, the carbon dioxide expelled by boiling, orange coloured sodium uranate precipitated with sodium hydroxide, the precipitate filtered off, washed with a little hot water, and dried. The filter paper is ignited in a platinum crucible, the dried uranate added, the contents of the crucible strongly ignited, and, when cold, brought on to a small filter paper; the free alkali contained in the uranate is washed out with hot water, the filter paper and contents again dried, ignited, and the pure sodium uranate (uranium yellow) weighed. 100 parts $Na_2U_2O_7$ = 88·55 parts U_3O_8.

According to C. Winkler, the results obtained in the analysis of ores rich in copper are somewhat too high, on account of a small amount of unprecipitated copper being carried over into the alkaline solution.

H. Bornträger [1] found that in the analysis of poor ores, and especially of uranium sands, considerable quantities of silica (up to 4 per cent.) are contained in the sodium uranate, and advises the solution of the uranium precipitate in hydrochloric acid, the filtering off of the silica, the precipitation of the uranium in the filtrate with ammonia, and finally weighing it as U_3O_8 (*cf.* Method 1).

3. Determination of Uranium in Ores containing Phosphorus and Arsenic (R. Fresenius and E. Hintz).[2]

The silica is separated as usual from the nitric acid, hydrochloric acid, or aqua regia solution, excess of potassium ferrocyanide added to the dilute hydrochloric acid solution, and the solution then saturated with sodium chloride. The precipitate, containing uranium, copper, and iron

[1] *Z. anal. Chem.*, 1898, **37**, 436; *J. Soc. Chem. Ind.*, 1898, **17**, 1184.

[2] *Z. anal. Chem.*, 1895, **34**, 437; *J. Chem. Soc. Abstr.*, 1895, **68**, 536; *cf.* also E. F. Kern, *J. Amer. Chem. Soc.*, 1901, **23**, 685; *J. Soc. Chem. Ind.*, 1901, **20**, 1144.

ferrocyanides, which soon settles, is first washed by decantation, and then on the filter paper with water containing sodium chloride, and is then treated with dilute potassium hydroxide without warming. When the decomposition of the ferrocyanides is complete and the hydrated oxides have settled, the solution is poured through a filter paper, the precipitate again washed once by decantation with water, and the hydrated oxides transferred to the filter paper with water containing ammonium chloride and ammonia, with which they are washed uninterruptedly until the filtrate, on acidifying, shows no traces of potassium ferrocyanide.

The hydrated oxides are then treated with hydrochloric acid. If the foregoing operations have been properly carried out, they are completely dissolved. Should an insoluble residue of ferrocyanides remain, after washing, it must be again treated with potassium hydroxide, etc., as described above.

The solution of metallic chlorides contains no phosphoric or arsenic acids, if the precipitate of the ferrocyanides has been well washed; it is concentrated, and if necessary the greater part of the free acid is neutralised with ammonia, to the clear solution a moderate excess of ammonium carbonate is added, and the solution allowed to stand for some time. The ferric hydroxide remaining undissolved is filtered off, washed with water containing some ammonium carbonate and the filtrate and washings heated so as to remove the greater part of the ammonium carbonate. The solution is then acidified with hydrochloric acid, whereby the yellow flocculent precipitate produced by boiling is redissolved, and sulphuretted hydrogen then passed into the hot solution to precipitate the copper. The copper sulphide is obtained free from uranium. The filtrate from the copper sulphide is concentrated, and the uranium precipitated with ammonia as hydrated uranium oxide, which is converted by ignition in an open crucible into U_3O_8, and weighed as such. As a check, the contents of the crucible are ignited in a current of hydrogen and the weight of uranous oxide also obtained.

According to published results, this method is to be recommended; it is specially suited to the analysis of ores containing uranium mica (phosphate) and uranium arsenate.

4. Analysis of Uranium-Vanadium Ores (Carnotite).

The details of analysis are described under Vanadium, p. 352.

VANADIUM

Vanadium is very widely diffused, though in inconsiderable quantities. It is found in many silicate rocks, particularly in those rich in magnesium and iron, also in clays, bauxites, in many oolitic brown hæmatites, and even in lignites. The extraordinarily high percentage of 38·5 per cent. of vanadic acid has been found in the ash of a lignite from San Rafael, Province Mendoza, Argentine.

The best known ores with a high content of the metal are: *Vanadinite*, $3Pb_3(VO_4)_2,PbCl_2$, containing up to 19·3 per cent. of vanadium pentoxide, and *Descloizite* (often found associated with vanadinite), a hydrated lead zinc vanadate with up to 22·7 per cent. Other important sources of the metal are: *Mottramite*, a hydrated lead copper vanadate containing up to 18·8 per cent. of vanadium pentoxide; *Roscoelite*, or *Vanadium mica*, containing up to 24 per cent.; *Carnotite*, a hydrated potassium uranyl vanadate with 15 to 18 per cent.; *Patronite*,[1] a mixture of vanadium sulphide with molybdenum trioxide, silica, alumina, and oxides of iron, etc., containing up to 10 per cent. of vanadium; and *Anthracite* (*Asphaltite*) rich in sulphur, which occurs in the Quisque and Yauli districts in Peru, and contains up to 1·5 per cent. of vanadium pentoxide. All these raw materials, including the ash of lignites, serve for the manufacture of vanadium preparations, chiefly ferro-vanadium. This alloy comes on the market with up to 50 per cent. of vanadium, and may be obtained, either free from, or containing carbon.

A. Detection of Vanadium in Minerals and Rocks

Vanadium is detected in high grade minerals by moistening with a drop of strong hydrochloric acid, when a deep red colour rapidly changing to green indicates its presence. The same test may be carried out by treating a few pieces of the mineral, contained in a beaker with strong hydrochloric acid. The deep red colour forms at once when vanadium is present but soon changes to a deep green colour, especially on heating; it is restored by the addition of hydrogen peroxide.

For the detection of very small quantities of vanadium [2] in minerals, rocks or slag, 5 g. of the finely pulverised material is fused over the blowpipe with a mixture of 20 g. of sodium carbonate and 3 g. of sodium nitrate. The mass is extracted with hot water, some alcohol added to

[1] *Cf.* D. F. Hewett, *Trans. Amer. Inst. Min. Eng.*, 1909, p. 291; *J. Iron and Steel Inst.*, 1909, **80**, 337.

[2] W. Hillebrand, *J. Amer. Chem. Soc.*, 1898, **20**, 209; *Chem. News*, 1898, **78**, 216; Treadwell and Hall, *Analytical Chemistry*, vol. i., p. 490.

reduce any manganate formed, the solution filtered, the filtrate almost neutralised with nitric acid (the necessary quantity of the acid is found by a blank experiment), evaporated nearly to dryness, taken up with water, and filtered. The filtrate, which must be alkaline, is mixed with mercurous nitrate solution, which may cause a precipitate of mercurous phosphate, arsenate, chromate, molybdate, tungstate, and vanadate, as well as of much basic mercurous carbonate. The liquid is boiled, filtered, the precipitate dried, detached from the filter paper, and heated in a platinum crucible in a draught cupboard. The residue is ignited and fused with a very small quantity of sodium carbonate and extracted with water; a yellow colour of the solution indicates the presence of chromium. The solution is acidified with sulphuric acid, and traces of platinum, molybdenum and arsenic precipitated by sulphuretted hydrogen in a pressure bottle; the precipitate is filtered off, the sulphuretted hydrogen boiled off, the filtrate evaporated down until almost all the sulphuric acid is expelled, and the residue dissolved in 2 or 3 c.c. of water; a few drops of hydrogen peroxide solution are then added, when a brownish yellow coloration shows the presence of vanadium.

In order to detect vanadic acid in the presence of chromic acid, E. Champagne[1] recommends shaking the solution, which has been acidified with sulphuric acid, with hydrogen peroxide and ether. A blue coloration of the ethereal layer indicates chromium, while a yellow coloration (brownish yellow if considerable quantities are present) of the aqueous solution shows the presence of vanadium.

In the colorimetric test for vanadium by means of hydrogen peroxide interference may arise through the presence of titanium or iron. A few drops of hydrofluoric acid will remove the colour due to titanium and a few c.c. of phosphoric acid, that due to iron.

B. Methods of Analysis

Volumetric Methods

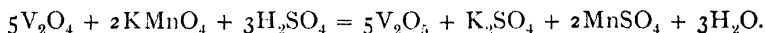
These methods are always employed, as they are both rapid and very accurate.

1. Titration of Vanadyl sulphate with Potassium permanganate.

Vanadic acid in a solution acidified with sulphuric acid is at once reduced to the tetroxide by sulphuretted hydrogen, or by sulphur dioxide. After boiling off the reducing agent, the dilute bluish solution, which should be at a temperature of about 70°, is titrated with dilute permanganate, whereby re-oxidation to the pentoxide occurs.

[1] *Ber.*, 1903, 36, 3164.

The end-point is shown by a reddish coloration. The reaction is represented by the following equation:—

$$5V_2O_4 + 2KMnO_4 + 3H_2SO_4 = 5V_2O_5 + K_2SO_4 + 2MnSO_4 + 3H_2O.$$

The iron value of the permanganate solution, multiplied by 1·632 gives the vanadium pentoxide, or, multiplied by 0·916, the vanadium.

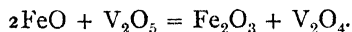
The vanadium solution should contain from 0·1 to 0·2 g. of the pentoxide and a few cubic centimetres of sulphuric acid in 500 c.c. The solution is mixed with about 30 c.c. of freshly prepared, saturated sulphurous acid solution, warmed, boiled, and the removal of the sulphur dioxide accelerated by passing in carbon dioxide. After boiling for half an hour, the escaping gases are tested for sulphur dioxide by passing them through a test tube of water rendered faintly pink by permanganate, which should not be decolorised (Treadwell). The reaction with starch iodide paper is less sensitive.

Hillebrand and Ransome (*cf.* Ore Analysis, 1 (*b*), p. 352) have observed that old solutions of sulphur dioxide in water, and also solutions of alkali sulphites, contain other oxidisable substances besides sulphur dioxide, which are not removed from the solution acidified with sulphuric acid even by prolonged boiling.

Sulphuretted hydrogen is not usually employed as the reducing agent; the filtrate from the copper, lead, and arsenic precipitate obtained in the course of the analysis can, however, be titrated with permanganate after boiling off the sulphuretted hydrogen (*cf.* Ore Analysis, 1 (*b*)), The titration can be repeated after passing sulphur dioxide through the solution, which has been cooled after titration (or a fresh addition of aqueous sulphurous acid can be made), and boiling off the excess.

2. Titration of Vanadic acid with Ferrous sulphate (Lindemann).

Lindemann reduces the pentoxide to tetroxide in a cold solution, slightly acidified with sulphuric acid, with a solution of ferrous sulphate (or ferrous ammonium sulphate) which has been recently standardised by permanganate; potassium ferricyanide solution is used as the indicator. The reduction takes place in accordance with the equation:—

$$2FeO + V_2O_5 = Fe_2O_3 + V_2O_4.$$

Hence 55·84 parts of ferrous iron correspond to 50·96 parts of vanadium.

The solution of vanadic acid, oxidised exactly according to Lindemann's directions, is diluted to 300 c.c., and one-third of the solution used in a preliminary experiment to determine the approximate volume of ferrous sulphate solution required. The titration is repeated with half

of the remaining solution, and the residual third is used for a control determination. Chromium contained in the original substance is finally present as chromic chloride, which is not altered by permanganate. A special advantage of this method is that the presence of ferric iron in the vanadium solution does not affect the result.

In the analysis of an ore, for instance, the vanadic acid can be accurately determined in presence of the generally small quantity of iron, in the solution obtained by decomposition with hydrochloric acid or aqua regia after it has been freed from lead, copper, arsenic, and molybdenum by sulphuretted hydrogen, and the filtrate evaporated down and oxidised with potassium chlorate. In the titration with permanganate (Method 1), on the other hand, the ferrous salt present is titrated as well, and an iron estimation is required to correct the result. Since, to separate iron and vanadium, repeated treatment with alkali hydroxide is necessary in order to obtain vanadium-free ferric hydroxide, this applicability of Lindemann's method is especially valuable.

C. Special Methods for Ores

1. Analysis of Vanadium Ores[1] (Vanadinite, Descloizite, Cupro-descloizite, Mottramite), in the absence of Chromium.

A suitable quantity of the average sample of the ore is decomposed with acids, or if necessary by fusion with potassium bisulphate (quantity not to exceed 10 g.) and the solution obtained filtered if necessary. Ten c.c. of strong sulphuric acid (or 20 c.c. if much soluble matter other than vanadium is present) is added and the whole heated until fumes appear. After cooling, a small quantity of powdered potassium permanganate is added and the solution again heated to destroy organic matter, and then allowed to cool. Hydrogen peroxide solution free from organic matter and preferably containing 3 per cent. H_2O_2 or more is added drop by drop until the excess of permanganate is decomposed. The solution is heated until fumes begin to appear, is then allowed to become quite cold and is subsequently treated by a method dependent on whether basic salts have separated, soluble salts have crystallised out, or the solution remains clear.

(*a*) If no salts have separated, 1 c.c. of hydrogen peroxide[2] solution is added drop by drop from a pipette with constant agitation of the solution. The excess of hydrogen peroxide thus introduced is catalytically decomposed in a few seconds by the vanadyl sulphate solution in strong sulphuric acid and no further heating is required. It is advisable

[1] A. W. Hothersall, *J. Soc. Chem. Ind.*, 1924, 43, 270T.
[2] Cain and Hostetter, *J. Amer. Chem. Soc.*, 1912, 34, 274.

however, to allow the solution to stand for 10 to 15 minutes, after which it is diluted to 300 c.c., heated to 70° and titrated with standard potassium permanganate.

(*b*) If salts have separated, water sufficient to dissolve them, but not more than twice the volume of strong sulphuric acid present, is added and the whole warmed until solution is complete. After cooling to room temperature, 5 c.c. of hydrogen peroxide solution followed by a few crystals (say 0·1 g.) of potassium bromide are added. The flask is covered with a watch glass and the solution set aside for twenty-four hours, after which, in order to remove bromine and hydrobromic acid, it is heated until fumes appear.

After cooling, a little water is added and the solution warmed to dissolve separated salts, diluted to 350 c.c. (or to 700 c.c. if much iron is present), heated to 70° and titrated with standard potassium permanganate solution, a few c.c. of syrupy phosphoric acid being added to remove the iron colour if necessary.

Whether reduction is conducted in strong acid solution (*a*) or dilute acid solution (*b*), in the presence of large amounts of copper, iron, or other elements giving coloured sulphate solutions, it is advisable to make blank determinations.

Chromium interferes seriously with the determination and should be absent; molybdenum and uranium do not interfere.

2. Analysis of Uranium-Vanadium Ores (Carnotite).[1]

(a) *A. N. Finn's Method.*[2]—A quantity of the average sample which does not contain more than 0·25 g. of U_3O_8 is weighed out, decomposed with hot sulphuric acid (1 : 5), and the solution evaporated until fumes of the acid begin to be evolved. After cooling, the residue is taken up with water and boiled with an excess of sodium carbonate solution until the precipitate settles well. The precipitate is filtered off, washed, dissolved in the smallest possible quantity of dilute sulphuric acid, and again precipitated. The united filtrates and washings are acidified with sulphuric acid, 0·5 g. of ammonium phosphate added, boiled, made alkaline with ammonia, boiled again for a few minutes, and the precipitate of ammonium uranyl phosphate, which contains all the uranium, washed with hot water containing some ammonium sulphate.

The vanadium is titrated in the filtrate, with permanganate, after acidifying with sulphuric acid, followed by treatment with sulphur dioxide and removal of the excess by boiling or by reduction with hydrogen peroxide as described above.

The uranium precipitate is dissolved in sulphuric acid, an ample quantity of granulated zinc added, and the reduction allowed to

[1] *Cf.* C. E. Scholl, *Ind. Eng. Chem.*, 1919, **11**, 842.
[2] *J. Amer. Chem. Soc.*, 1906, **28**, 1443.

proceed for half an hour; the solution is then filtered on the pump through an asbestos filter to separate zinc (and finely divided lead), and the uranyl sulphate solution warmed to about 60° and titrated with *N*/20 permanganate.[1] The iron value of the permanganate multiplied by 2·133 gives the uranium, or multiplied by 2·5167, the uranoso-uranic oxide U_3O_8.

(b) *Method of Ledoux & Co.*[2]—One gram of the ore, previously finely powdered and dried at 100°, is gently heated in a small beaker with 25 c.c. of dilute nitric acid (1 : 3), the solution filtered, and the residue washed with hot water. The filtrate is diluted, the lead, copper, etc., precipitated by sulphuretted hydrogen, the solution filtered, and the filtrate boiled to remove the excess of sulphuretted hydrogen. Hydrogen peroxide is then added to oxidise the iron and the excess decomposed by boiling. The solution, which contains all the uranium and vanadium, is allowed to cool, neutralised with ammonia, an ample quantity of saturated ammonium carbonate solution added, and, after heating gently for a quarter of an hour, the ferric hydroxide precipitate filtered off. Since this precipitate retains some uranium and still more vanadium, it is dissolved in the smallest possible quantity of dilute nitric acid and reprecipitated. If it still gives the vanadium reaction when a few drops of hydrogen peroxide are added to its solution in nitric acid, the precipitation must be repeated once more. The united filtrates and washings are boiled in a large beaker to remove ammonia and ammonium carbonate, the solution finally becoming turbid by separation of uranium and vanadium compounds; this turbidity is removed by adding nitric acid, drop by drop, to the boiling solution. The beaker is then removed from the flame, 10 c.c. of a cold, saturated solution of lead acetate and a few grams of sodium acetate immediately added in order to precipitate the lead vanadate completely. The heating is continued for a short time on the water bath until the precipitate has settled, when it is filtered off and washed with hot water slightly acidified with acetic acid. No vanadium is contained in the filtrate, but the lead vanadate may retain some uranium. The precipitate is washed from the filter paper into a beaker, and dissolved, together with the residue on the filter paper, in the smallest possible quantity of nitric acid, the solution diluted, a few cubic centimetres of lead acetate solution and a sufficient quantity of sodium acetate (5 to 10 g.) added, and the lead vanadate, now free from uranium, filtered off. The filtrate is united with that first obtained and kept for the determination of the uranium.

For the determination of the vanadium, the lead vanadate is dissolved in nitric acid, and the lead removed from the solution by adding excess of sulphuric acid and filtering. The filtrate is boiled

[1] Bélohonbek's method, *Z. anal. Chem.*, 1872, 11, 179.
[2] A. H. Low, *Technical Methods of Ore Analysis*, 1905, p. 204.

down in a flask until the sulphuric acid is evaporated off, taken up with water, sulphur dioxide passed in, the excess boiled off, and the vanadium tetroxide titrated with permanganate. (*Cf.* The Volumetric Determination of Vanadium, p. 349.)

To the solution kept for the determination of uranium, 10 c.c. of concentrated sulphuric acid is added, and the lead sulphate filtered off. The filtrate is made slightly alkaline with ammonia, boiled, the ammonium uranate which settles collected on a filter paper, and, without washing the precipitate, dissolved at once in dilute sulphuric acid (1 : 6). The solution is boiled down in a flask until sulphuric acid fumes begin to be evolved, and finally, after reduction with zinc (*cf.* Finn's method, p. 352), the uranyl sulphate is titrated with permanganate by Bélohonbek's method (p. 353).

The determination of vanadium in pig iron, steel, and ferro-vanadium is described in the section on Iron and Steel, p. 77.

MOLYBDENUM

The most commonly occurring minerals used for the manufacture of molybdenum preparations and of the metal, which is employed for special steels, and for the alloy with iron (ferro-molybdenum) are:—*Molybdenite*, MoS_2, and *Wulfenite*, $PbMoO_4$. The following minerals occur to a more limited extent:—*Molybdite*, MoO_3; *Ilsemannite*, Mo_3O_8; *Molybdurane*, $UO_2 . UO_3 . 2MoO_4$; *Molybdoferrite*, $FeMoO_4$; *Peteraite*, $FeCoMo_2O_8$; *Eosite*, $Pb_3V_2MoO_{16}$. The slags of the Mansfeld Copper Works also contain a considerable proportion of molybdenum.

Detection of small quantities of Molybdenum in Ores, etc.

A few centigrams of the fine powder is heated on a porcelain lid with one drop of nitric acid and a few drops of distilled sulphuric acid until it fumes strongly; molybdenum, if present, dissolves as oxide, producing a deep blue colour.

METHODS OF ANALYSIS

The following are some of the analytical methods for molybdenite and wulfenite, which have been proved to be satisfactory:—

1. Determination of Molybdenum in Molybdenite.

Molybdenum Sulphide Method.—Five grams of a finely powdered good average sample is boiled down in an Erlenmeyer flask with 50 c.c. of concentrated nitric acid to about 10 c.c., the residue carefully taken

up with ammonia, and warmed until all the molybdenum trioxide is dissolved. The solution is then washed into a litre flask, mixed with 50 c.c. of strong ammonium sulphide solution, and sulphuretted hydrogen passed in until the solution acquires a deep brown-red colour. The solution is now made up to the mark, well shaken, and an aliquot part, corresponding to about 0·5 g. of the substance, filtered through a dry filter. Molybdenum sulphide and sulphur are then precipitated by adding a slight excess of dilute sulphuric acid, filtered off, washed with hot water, dried, the filter paper incinerated in a Rose's crucible at a moderate temperature, the sulphide and a little sulphur added, heated, and finally ignited for a quarter of an hour in a current of hydrogen. $MoS_2 \times 0{\cdot}5996$ = Molybdenum.

Note.—Molybdenite should be nearly pure, and contain as little as possible of other sulphides, especially sulphide of copper.

2. Determination of Molybdenum in Wulfenite.

(*a*) *Sulphuric Acid Method.*[1]—Half a gram of the substance, in the form of very fine powder, is heated for about twenty-four hours on a boiling water bath, with 25 c.c. of sulphuric acid of sp. gr. 1·25, to which a few drops of nitric acid have been added. The solution is diluted with water, filtered, and the residue washed with water containing sulphuric acid. The filtrate from the lead sulphate is mixed with excess of ammonia, ammonium sulphide added, sulphuretted hydrogen passed in for a long time, and the analysis completed as in Method 1.

In principle this method corresponds to that of C. Friedheim.[2]

(*b*) *Method of the Bleiberg Mines Union, Klagenfurth, for Wulfenite, Slags, and Residues containing Lead.*—Half a gram of the finely powdered substance is heated for about an hour with nitric acid, diluted with its own volume of water, in a covered porcelain basin on a sand bath. A few cubic centimetres of sulphuric acid is then added, the mixture evaporated on the water bath, and finally on the sand bath, until sulphuric acid fumes are evolved, then diluted with water, the precipitate allowed to settle, filtered off, and washed with water containing sulphuric acid. The filtrate is diluted to 500 to 600 c.c., excess of ammonia and then 25 c.c. of yellow, freshly prepared ammonium sulphide added, filtered, heated, and dilute hydrochloric acid added, drop by drop, until the reaction is just acid. After boiling for a quarter of an hour, the very voluminous precipitate should settle quickly, and the liquid be quite colourless. A blue or brown colour shows the presence of molybdenum, which must be precipitated by

[1] Private communication from Dr C. Ahrens to Prof. Pufahl.

[2] Cf. *Ber.*, 1895, **28**, 2061; 1896, **29**, 2981; *J. Soc. Chem. Ind.*, 1896, **15**, 220; 1897, **16**, 263.

sulphuretted hydrogen. The precipitate is filtered off, washed with hot water, dried, and separated from the filter paper, which is ignited by itself in a porcelain crucible. The precipitate is then added, the sulphur carefully burnt off, and the residue heated, at first gently, and finally more strongly, until the whole mass is converted into long yellowish white crystals of molybdic acid.

(*c*) *Fusion Method.*—This method is applicable to both wulfenite and molybdenite. One-half to one gram of the finely ground ore, dried at 100°, is fused in a porcelain crucible with six times the weight of sodium carbonate and sulphur. The fusion is extracted with water the solution filtered, acidified with hydrochloric acid, warmed for some time, the very bulky molybdenum sulphide precipitate containing sulphur filtered through a weighed filter paper, and dried till constant. A weighed portion of this precipitate is then strongly ignited in a Rose crucible in a current of hydrogen; the sulphide is thus converted into the black sulphide MoS_2, and is weighed as such. $MoS_2 \times 0{\cdot}5996$ = Molybdenum.

3. Determination of Molybdenum in Ferro-molybdenum and in Molybdenum steel.

Cf. the section on Iron and Steel, p. 75.

LITERATURE

BERINGER, C. and J. J.—*Text-book of Assaying*, 15th edition, 1921.
BREARLEY, H., and IBBOTSON, F.—*The Analysis of Steel-works Materials*, 1902.
CLENNEL, J. E.—*The Chemistry of Cyanide Solutions resulting from the Treatment of Ores*, 1904.
FRESENIUS, R.—*Quantitative Chemical Analysis*, 7th edition; vol. i. translated by A. Vacher, 1876; vol. ii. translated by C. E. Groves, 1900.
IBBOTSON, F., and AITCHISON, L.—*The Analysis of Non-ferrous Alloys*, 1915.
LOW, A. H.—*Technical Methods of Ore Analysis*, 1908.
MOORE, R. B.—*Analytical Methods for Certain Metals*, Bulletin 212, Bureau of Mines, Washington, 1923.
OHLY, J.—*Rare Metals*, 1907.
PARRY, L.—*The Assay of Tin and Antimony*, 1907.
RHEAD, E. L., and SEXTON, A. H.— *Assaying and Metallurgical Analysis*, 1914.
RICKETTS, P., and MILLER, E. H.—*Notes on Assaying*, 1902.
SCHOELLER, W. R., and POWELL, A. R.—*The Analysis of Minerals and Ores of the Rarer Elements*, 1919.
SCOTT, W. W.—*Standard Methods of Chemical Analysis*, 4th edition, 1925.
SCOTT, W. W.—*Standard Methods of Metallurgical Analysis*, 1923.
SMITH, E. A.—*Sampling and Assay of the Precious Metals*, 1913.
SUTTON, F.—*Volumetric Analysis*, 11th edition, 1924.
TREADWELL, F. P.—*Analytical Chemistry*, translated from the German by W. T Hall, 5th edition, 1919.
WRAIGHT, E. A.—*Assaying in Theory and Practice*, 1914.

METALLIC SALTS[1]

By W. R. SCHOELLER, Ph.D., Metallurgical Chemist, London.

POTASSIUM SALTS

(*See Separate Section*, p. 399)

SODIUM SALTS

Sodium Sulphate.—See Vol. I., pp. 509-514.

Sodium Thiosulphate, $Na_2S_2O_3+5H_2O$ (*Sodium Hyposulphite*).—The pure salt forms colourless, prismatic crystals which melt in their water of crystallisation at 48·5°; they lose all their water at 215°, and decompose at 223° with separation of sulphur. One hundred parts of water dissolve:—

°C.	Parts $Na_2S_2O_3$.	°C.	Parts $Na_2S_2O_3$.
10	61	60	206·7
20	70	80	248·8
30	84·7	90	254·9
40	102·6	100	266
50	169·7		

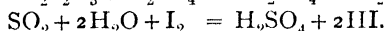
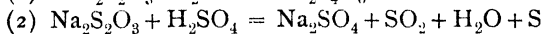
According to Schiff, the specific gravity of solutions at 19° is as follows:—

Per cent. $Na_2S_2O_3$ $5H_2O$.	Sp. gr.	Per cent. $Na_2S_2O_3$ $5H_2O$.	Sp. gr.	Per cent. $Na_2S_2O_3$ $5H_2O$.	Sp. gr.
1	1·0052	10	1·0529	35	1·1986
2	1·0105	15	1·0807	40	1·2297
3	1·0158	20	1·1087	45	1·2624
4	1·0211	25	1·1381	50	1·2954
5	1·0264	30	1·1676		

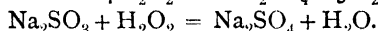
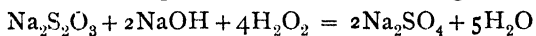
[1] The writer is indebted to Messrs Thomas Tyrer & Co., Ltd., for information concerning the commercial varieties and usual impurities of many additional salts described in this Edition.

The salt is used in photography as a solvent for silver salts, on a large scale as "antichlor" in the manufacture of paper, and in dyeing and tanning. The commercial salt, in the form of pea crystals, is generally very pure; it should contain 99 per cent. of the pentahydrate. The chief impurities are moisture, sulphate, and small quantities of other sulphur compounds. For photographic purposes, the salt should be quite free from sulphide, which is ascertained by the lead paper test or by addition of silver nitrate solution, which must give a white precipitate free from any dark tint. A 5 per cent. solution should give no immediate turbidity with ammonium oxalate (absence of lime). The same solution, treated with a slight excess of iodine followed by barium chloride solution, should remain clear (freedom from sulphate and sulphite).

Analysis. (1) A measured volume of dilute thiosulphate solution is titrated with $N/10$ iodine solution. (2) The same quantity of the solution is then distilled with sulphuric acid into an excess of $N/10$ iodine, and the excess of the latter titrated with $N/10$ thiosulphate solution. The thiosulphate consumes twice as much iodine in the second as in the first operation, while any sulphite present requires the same amount in each titration:—

$$(1)\quad 2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$
$$(2)\quad Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + SO_2 + H_2O + S$$
$$SO_2 + 2H_2O + I_2 = H_2SO_4 + 2HI.$$

If the volume of iodine used in the first titration $= a$ c.c., and that in the second titration $= b$ c.c., then $(b-a)$ c.c. correspond to the thiosulphate, and $(2a-b)$ c.c. to the sulphite present.

Alternatively, the thiosulphate may be determined by warming the solution with a measured excess of standard alkali and hydrogen peroxide, and titrating the excess alkali with standard sulphuric acid. Sulphite is oxidised to sulphate without consuming alkali:—

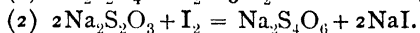
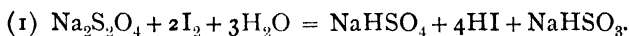
$$Na_2S_2O_3 + 2NaOH + 4H_2O_2 = 2Na_2SO_4 + 5H_2O$$
$$Na_2SO_3 + H_2O_2 = Na_2SO_4 + H_2O.$$

For the estimation of sulphide, a solution of the salt is treated with cadmium acetate in the presence of a little acetic acid. The precipitate is filtered off and washed; the precipitate and filter are stirred into 20 c.c. of hydrochloric acid (1 : 1), and the liquid is titrated with $N/10$ iodine solution.

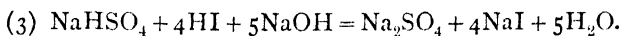
Sodium Hyposulphite, $Na_2S_2O_4 + 2H_2O$ (*Sodium Hydrosulphite, Blankit*).—The pure salt crystallises in needles, soluble in about 5 parts of water. On exposure to the air, both the solid salt and its aqueous solution oxidise rapidly to bisulphite. The salt is used extensively for bleaching, in indigo vat-dyeing, and in the manufacture of drugs and dyestuff intermediates.

Analysis.[1] Interference of atmospheric oxygen is counteracted by

[1] De Bacho, *Z. anal. Chem.*, 1922, 61, 209; see also Merriman, *Chem. and Ind.*, 1923 (*J. Soc. Chem. Ind.*, 42), 290.

titration in presence of formaldehyde. One g. of the salt is dissolved in 5 c.c. of water and 10 c.c. of pure concentrated formaldehyde solution in the weighing bottle. The stoppered bottle must be left to stand for twenty minutes. The solution is then rinsed into a graduated 500 c.c. flask and treated with 200 c.c. of water free from carbon dioxide, 2 drops of 0·1 per cent. methyl orange, and just sufficient *N* sulphuric acid to produce the pink tinge. The liquid is diluted to 500 c.c. with boiled water, and 50 c.c. treated with phenolphthalein and *N*/10 alkali (free from carbonate) to faint pink; the solution is now titrated with *N*/10 iodine (free from hydriodic acid) and starch. Neither bisulphite nor pyrosulphite (metabisulphite) interferes in presence of excess of formaldehyde; but neutral sulphite is converted into bisulphite by the above procedure. On the other hand, thiosulphate, which is always present, causes high results:—

$$(1)\ Na_2S_2O_4 + 2I_2 + 3H_2O = NaHSO_4 + 4HI + NaHSO_3.$$
$$(2)\ 2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

The solution, after titration with iodine, is therefore decolorised with a drop of thiosulphate solution and titrated with *N*/10 alkali free from carbonate; the acidity is a measure of the hyposulphite:—

$$(3)\ NaHSO_4 + 4HI + 5NaOH = Na_2SO_4 + 4NaI + 5H_2O.$$

The bisulphite formed in equation (1) does not interfere, as it combines with the formaldehyde. The amount of thiosulphate present is found by multiplying the number of cubic centimetres of *N*/10 alkali by 0·8 and subtracting the product from the number of c.c. of *N*/10 iodine solution. The difference corresponds to the thiosulphate. One c.c. *N*/10 iodine solution = 0·004352 g. $Na_2S_2O_4$.

Sodium chloride is a frequent impurity of commercial hyposulphite. The solution, after standing some time, is acidified with nitric acid and tested with silver nitrate.

Sodium Sulphide, $Na_2S + 9H_2O$, forms large white crystals which melt in their water of crystallisation at 48°. According to Parravano and Fornaini the saturated solution contains:—

at	10°	22°	32°	45°	
	13·36	16·20	19·09	24·19	per cent. Na_2S.

The specific gravity of solutions of the salt is given by Bock as follows:—

Per cent. Na_2S.	Sp. gr.	Per cent. Na_2S.	Sp. gr.
2·02	1·0212	14·02	1·1583
5·03	1·0557	16·12	1·1810
9·64	1·1102	18·15	1·2158

Sodium sulphide is made on the large scale and is used in the manufacture of soluble soda glass, as a depilatory in tanning, for the preparation of sulpho-dyes, as a reducing agent for nitro-compounds, and as sheep dip.

Four varieties are found in commerce: (1) *fused commercial*, containing usually 60 to 65 per cent. of Na_2S with small amounts of sodium sulphate and iron; (2) *commercial crystal*, generally brown and containing a little iron and polysulphides; (3) *crystal pure*, large colourless, transparent crystals; and (4) *sulphated soda*, a complex mixture of polysulphide, thiosulphate, sulphate, carbonate, and sulphite; it contains about 45 to 50 per cent. of total sulphur, and finds application in agriculture.

A solution of 5 g. of "crystal pure" salt in 10 c.c. of water should be perfectly clear. A 5 per cent. solution, acidified with hydrochloric acid, should show only a slight opalescence (absence of other sulphur compounds). A black residue insoluble in water usually consists of ferrous sulphide, sometimes containing silica.

Analysis. Ten g. is dissolved in water; the solution is filtered and diluted to 1000 c.c.; the residue is dissolved in hydrochloric acid, the solution reduced with zinc, and titrated with permanganate for iron.

(*a*) Estimation of sulphide: 100 c.c. of the filtrate is treated with acetic acid till weakly acid and titrated with $N/10$ iodine solution. Another portion of 100 c.c. is treated with cadmium carbonate to eliminate the sulphide; the clear filtrate is again titrated with iodine solution. The difference between the two readings gives the iodine corresponding to the sulphide, while the second titration determines the thiosulphate present.

(*b*) Sodium carbonate: 100 c.c. of the filtrate is titrated with $N/2$ hydrochloric acid and methyl orange, and the amount of acid consumed by sodium sulphide is calculated from (*a*). The difference is calculated to sodium carbonate.

(*c*) Total sulphur: 100 c.c. of the filtrate is oxidised with hydrogen peroxide or bromine to sulphate which is then precipitated in the usual manner with barium chloride. The difference between total sulphur and sulphide *plus* thiosulphate sulphur is calculated to sodium sulphate.

Sodium Nitrite, $NaNO_2$, crystallises in four-sided prisms, melting at 271°. One hundred parts of water dissolve:—

°C.	Parts $NaNO_2$.	°C.	Parts $NaNO_2$.	°C.	Parts $NaNO_2$.
10	78	40	98·5	90	147
20	84	50	107	110	178
30	91·5	70	125·5	120	198·5

The salt is largely used for diazotising in the manufacture of coal-tar dyes (Germany consumed 10,000 tons in 1912).

The commercial salt contains 95 to 98 per cent. of $NaNO_2$, the usual impurities being nitrate and, occasionally, a little carbonate or sulphate. The solution of the commercial article is generally alkaline, though the pure salt is neutral. A 5 per cent. solution, acidified with nitric acid, should give no immediate precipitate with barium chloride or silver nitrate; it should not darken on addition of strong hydrogen sulphide water (absence of lead).

Analysis.[1] The only quantitative estimation usually required is that of the nitrite. A solution containing a weighed quantity of the salt is run from a burette into a measured volume of standard permanganate solution, acidified with sulphuric acid, until the colour is just discharged. The permanganate solution is standardised in a similar manner against pure silver nitrite twice recrystallised from water. The purity of this salt may be checked by ignition, and weighing the residual silver. Sodium nitrite for use in dye manufacture may also be standardised against pure sulphanilic acid (see Organic Dyes, Vol. IV.).

If lead is found by the qualitative test, it may be determined by boiling a solution of 2 g. of the salt with sulphuric acid and evaporation to fumes. The cold acid is diluted with water and the lead sulphate filtered off and estimated in the usual manner. (See p. 226.)

Sodium Silicate occurs in commerce as glassy transparent lumps, prepared by fusion of an equimolecular mixture of sodium carbonate and quartz sand. The material dissolves only very slowly even in hot water, but the rate of solution is rapidly increased by heating under pressure. The salt is usually sold as a viscous mass (water-glass), made by boiling kieselguhr with caustic soda under pressure and evaporating the liquid to the desired consistency—*i.e.* a sp. gr. of about 1·7. At this stage the mass has the following composition : SiO_2 : 32 to 33 per cent., Na_2O : 16 to 16·5 per cent., other sodium salts 2·5 to 3 per cent., remainder water.

Water-glass is used as a cement in the manufacture of artificial stone, as an addition to toilet soaps, in the calico printing and dyeing industries, for fresco colours, and in stereochromy.

Analysis. Silica is determined gravimetrically by evaporation with hydrochloric acid in the usual manner. The total alkalinity is measured by titration with *N* acid in presence of methyl orange. For the estimation of free alkali the solution is diluted, treated with barium chloride solution, and filtered; the filtrate is titrated with *N* acid. Alternatively the solution is saturated with sodium chloride and an equal volume of alcohol added to precipitate sodium silicate; an aliquot part of the filtrate is then titrated as before.

[1] See also Höeg, *Analyst*, 1927, **52**, 433.

Sodium Phosphate (*disodium hydrogen phosphate*), $Na_2HPO4 + 12H_2O$, crystallises in colourless, transparent, efflorescent monoclinic prisms which melt in their water of crystallisation at 35°. At a red heat it is converted into pyrophosphate. One hundred parts of water, according to Mulder, dissolve the following quantities of anhydrous salt:—

°C.	Parts Na_2HPO_4.	°C.	Parts Na_2HPO_4.	°C.	Parts Na_2HPO_4.
0	2·5	40	63·9	80	96·6
10	3·9	50	82·5	90	97·8
20	9·3	60	91·6	99	98·8
30	24·1	70	95·0	106·4	79·2

The specific gravity of aqueous solutions at 19° has been determined by Schiff:—

Per cent. $Na_2HPO_4\,12H_2O$.	Sp. gr.	Per cent. $Na_2HPO_4\,12H_2O$.	Sp. gr.
1	1·0041	9	1·0376
3	1·0125	11	1·0460
5	1·0208	12	1·0503
7	1·0292		

The aqueous solution is alkaline to litmus. The salt is used in the manufacture of glazes, as a flux in soldering and welding, in calico printing, for weighting silk, and as an impregnating agent for rendering wood and fabrics fireproof. It is included in the British Pharmacopœia.

A 5 per cent. solution of the medicinal salt should give no immediate turbidity when acidified with hydrochloric acid and treated with barium chloride, or on treatment with nitric acid and silver nitrate; hydrogen sulphide water should cause no darkening of the solution. The limit laid down by the Pharmacopœia for lead and for arsenic is 5 parts per million (see Appendix, p. 397).

Analysis. The gravimetric estimation of phosphoric acid is unnecessary. A weighed amount of the salt is dissolved in water, and an aliquot part of the solution titrated with *N* acid in presence of methyl orange or cochineal. The end-point indicates the completion of the reaction $Na_2HPO4 + HCl = NaH_2PO4 + NaCl$.

Sodium Acetate, $CH_3CO_2Na+3H_2O$, forms colourless transparent prisms. One hundred parts of water dissolve, according to Schiavor:—

at	10°	20°	30°	40°	
	41	49	57	65	parts of anhydrous salt,

and the specific gravity of solutions at 17·5° (Gerlach) is:—

Per cent. $CH_3CO_2Na\,3H_2O$.	Sp. gr.	Per cent. $CH_3CO_2Na\,3H_2O$.	Sp. gr.
5	1·015	30	1·0960
10	1·031	35	1·1130
15	1·047	40	1·1305
20	1·063	45	1·1485
25	1·0795	50	1·1670

Sodium acetate becomes anhydrous at 120° and melts at 319°. It is used in the preparation of organic chemicals such as acetyl chloride, acetic anhydride, ethyl acetate, etc.; it comes into commerce as crystallised or fused (anhydrous) salt. Commercial sodium acetate usually contains small amounts of chloride, sulphate, lime, free alkali, and empyreumatic substances; a little iron and lead may also be present. Larger amounts of lead may be found in inferior samples. The purified salt should be odourless, free from the impurities mentioned above, and contain not less than 99·5 per cent. of the trihydrate Chloride, sulphate, and heavy metals are detected as directed under sodium phosphate (p. 362).

Analysis.—Acetic acid is estimated as explained under calcium acetate (p. 367). To determine lead, a solution of 5 to 20 g. of the salt in water is acidified with a little acetic acid, filtered if necessary, heated to boiling, and precipitated with potassium dichromate. The lead chromate may be ignited and weighed, or estimated iodimetrically.

MAGNESIUM SALTS

Magnesium Sulphate, $MgSO_4+7H_2O$ (*Epsom salts*) forms white, transparent needles free from efflorescence, dissolving in water to a neutral solution. One hundred parts of water dissolve (Mulder):—

°C.	Parts $MgSO_4$.	°C.	Parts $MgSO_4$.	°C.	Parts $MgSO_4$.
0	26·9	40	45·6	80	64·2
10	31·5	50	50·3	90	68·9
20	36·2	60	55·0	100	73·8
30	40·9	70	59·6	108·4	77·9

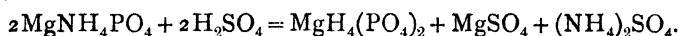
Schiff determined the specific gravity of solutions at 23° to be as follows:—

Per cent. $MgSO_4 7H_2O$.	Sp. gr.	Per cent. $MgSO_4 7H_2O$.	Sp. gr.	Per cent. $MgSO_4 7H_2O$.	Sp. gr.
1	1·0048	10	1·0487	35	1·1817
2	1·0096	15	1·0739	40	1·2108
3	1·0144	20	1·0997	45	1·2410
4	1·0193	25	1·1261	50	1·2722
5	1·0242	30	1·1536		

The salt is used in dyeing and for dressing cotton goods. It is taken internally as a purgative. The commercial article is sometimes deliquescent, due to the presence of 1 to 2 per cent. of magnesium chloride; sodium chloride is also a likely impurity. Lower grades containing much foreign matter are sold in sacks.

The medicinal salt must contain not more than a trace of iron and no zinc (ammonium sulphide test); it should be practically free from chloride. A solution of 10 g. in 20 c.c. of water should remain clear and colourless after one hour's heating in a closed flask on a steam bath. For lead or arsenic, the permissible maximum is 5 parts per million (see Appendix, p. 397). Oxalic acid and zinc sulphate have sometimes been sold for Epsom salts on account of their similarity in appearance.

For the estimation of magnesia in low-grade products, the weighed salt is dissolved in water. An aliquot part of the solution is heated to boiling and treated with bromine water, 5 g. of ammonium chloride, and ammonia in excess. Ammonium oxalate solution is added to the boiling filtrate: any lime present is removed by filtration. The filtrate is stirred and precipitated with sodium phosphate solution added drop by drop, followed by an excess of ammonia. After standing for some hours, the precipitate is filtered off, washed with 10 per cent. ammonia, and ignited to magnesium pyrophosphate. Alternatively, the washed precipitate may be washed free from ammonia with 50 per cent. alcohol, and dissolved in a known excess of $N/2$ acid; the excess is then measured with $N/2$ alkali in presence of methyl orange:

$$2MgNH_4PO_4 + 2H_2SO_4 = MgH_4(PO_4)_2 + MgSO_4 + (NH_4)_2SO_4.$$

Magnesium Chloride, $MgCl_2 + 6H_2O$, crystallises from hot, concentrated solutions as deliquescent needles. The salt decomposes above 186°, evolving water and hydrochloric acid and leaving a residue of oxide. One hundred parts of water dissolve:—

at	10°	100°	186°
	53·5	73	128 parts $MgCl_2$.

According to Gerlach, solutions of the salt at 15° have the following specific gravity:—

Per cent. $MgCl_2$.	Sp gr.	Per cent. $MgCl_2$.	Sp. gr.	Per cent. $MgCl_2$.	Sp. gr.
1	1·0084	5	1·0422	25	1·2274
2	1·0169	10	1·0859	30	1·2794
3	1·0253	15	1·1311	35	1·3340
4	1·0338	20	1·1780		

The salt is used for dressing cotton goods, for fireproofing, and in the manufacture of magnesium oxychloride cement.

The pure salt should give a clear solution in less than its own weight of water, and also in 90 per cent. alcohol; it should be free from sulphate, and addition of ammonium sulphide should not darken the solution. The chief impurities in the commercial salt are calcium and sodium chlorides and magnesium sulphate. Calcium is estimated by double precipitation with ammonium oxalate from a slightly ammoniacal solution containing excess of ammonium chloride. For the estimation of sodium, a solution of 2 g. of the salt is treated with a slight excess of barium hydroxide; the hot filtrate is acidified with hydrochloric acid, and the barium precipitated with sulphuric acid added drop by drop. The filtrate is evaporated to dryness, the residue dissolved in a few cubic centimetres of water, and the solution treated with ammonia and ammonium oxalate to remove lime. The filtrate is again evaporated to dryness; the residue is ignited in platinum, dissolved in water, the solution filtered, and evaporated to dryness with a few drops of sulphuric acid. The residue is ignited with a little ammonium carbonate to constant weight, and weighed as Na_2SO_4. Magnesium is determined as phosphate (see Magnesium Sulphate, p. 364) in the combined filtrates from the calcium oxalate precipitation. Chlorine and sulphuric acid are estimated as usual in separate portions taken for analysis.

Magnesium Carbonate occurs in commerce in two forms differing in density, but both consisting essentially of a basic carbonate $3MgCO_3 \cdot Mg(OH)_2$, with varying amounts of water. *Magnesia alba levis* is produced by precipitation of magnesium sulphate with sodium carbonate from a hot solution and has a density of about 1, whereas *magnesia alba ponderosa* is obtained by precipitation followed by evaporation to dryness, and has a density of about 3·5. Both varieties are white powders insoluble in water, alkaline to moist litmus paper, and readily and completely soluble in acids.

Magnesium carbonate for use in the preparation of effervescent salines must conform to the following tests. Three g. mixed with

50 c.c. of water and a slight excess of hydrochloric acid should give a perfectly clear liquid free from insoluble matter, which must not darken on treatment with excess of ammonia and a few drops of ammonium sulphide, nor give any immediate turbidity with ammonium chloride, hydroxide, and oxalate. The solution in nitric acid should give no chloride reaction with silver nitrate. The lead limit set by the Pharmacopœia is 20 parts per million, while the arsenic limit is 5 parts per million (see Appendix, p. 397).

Magnesium oxide may be estimated by ignition of a weighed quantity over a blast burner to constant weight. Both the light and heavy varieties lose from 56 to 58 per cent. of their weight.

SALTS OF THE ALKALINE EARTH METALS

Calcium Chloride, $CaCl_2+6H_2O$, crystallises in large hexagonal prisms, but the usual commercial article is the anhydrous salt in the form of granular, porous, deliquescent lumps. The hydrated salt melts at 30° in its water of crystallisation and becomes anhydrous above 200°; fusion takes place at 780°.

According to Roozeboom, 100 parts of water dissolve:—

°C.	Parts $CaCl_2$.	°C.	Parts $CaCl_2$.
0	59·5	60	136·8
10	65·0	80	147
20	74·5	100	159
40	115·3	170	255

The specific gravity of solutions at 15° has been determined by Gerlach:—

Per cent. $CaCl_2$.	Sp. gr.	Per cent. $CaCl_2$.	Sp. gr.	Per cent. $CaCl_2$.	Sp. gr.
1	1·0085	5	1·0426	25	1·2336
2	1·0170	10	1·0869	30	1·2879
3	1·0255	15	1·1336	35	1·3443
4	1·0341	20	1·1822	40	1·4033

The salt is readily soluble in alcohol.

Calcium chloride is produced in large quantities as a by-product in the manufacture of sodium carbonate, potassium chlorate, and chlorine by Weldon's process; it is used chiefly as a dehydrating agent. It occurs in three trade varieties: (*a*) *fused:* a white translucent mass

containing 20 per cent. of water, completely soluble in water; (*b*) *anhydrous:* white, porous, deliquescent fragments; nearly anhydrous, contains some basic salt, and dissolves to an alkaline solution; and (*c*) *crude:* large translucent brown blocks in sealed iron drums. This variety contains much basic salt and usually 1 to 2 per cent. of sodium chloride.

The crystallised salt should be completely soluble in water or alcohol; a 10 per cent. solution should give no turbidity with 20 c.c. of calcium sulphate solution after six hours (freedom from barium and strontium). Ammonium sulphide should produce no discoloration.

The only estimation usually required is the alkalinity of the dehydrated varieties. The weighed sample is dissolved in water and the solution titrated with *N*/10 hydrochloric acid in presence of phenolphthalein.

Calcium Acetate, $Ca(CH_3CO_2)_2 + 2H_2O$, forms white deliquescent crystals soluble in water or alcohol. One hundred parts of water dissolve (Lumsden):—

°C.	Parts $(CH_3CO_2)_2Ca$.	°C.	Parts $(CH_3CO_2)_2Ca$.
10	36·0	80	33·5
20	34·7	90	31·1
40	33·2	100	29·7
60	32·7		

Crude calcium acetate is the raw material for the manufacture of acetic acid and its derivatives and of acetone. The commercial article is very impure; the lumps, which also contain carbonate and sulphate, owe their greyish or brownish colour to the presence of empyreumatic matter.

The acetic acid content is estimated by distillation and titration of the distillate. Although the crude salt contains formate, propionate, and butyrate (the distillate containing 3 to 5 per cent. of these acids), the acidity found in the commercial assay is calculated to acetic acid. Four g. of the powder is treated with 200 to 250 c.c. of water and 20 c.c. of phosphoric acid (sp. gr. 1·6) in a 750 c.c. flask fitted for steam distillation and connected with a Liebig condenser. The flask is first heated by means of a flame, steam being applied later. When the distillate measures 750 c.c. the operation is interrupted; the distillate is titrated with *N* sodium hydroxide, with phenolphthalein as indicator. The phosphoric acid used must be free from nitric acid; if not, a few c.c. of ammonia are added, and the acid is heated to fusion in a platinum dish. If the calcium acetate contains chlorides, a hot solution of silver sulphate is added to the liquid in the distilling flask before distillation.

A typical sample of crude acetate has the following composition: calcium acetate, 82; moisture, 4; water of crystallisation, 10; inorganic and organic impurities, 4 per cent. The purified salt is occasionally used as a mordant in cotton printing.

Strontium Nitrate, $Sr(NO_3)_2$.—The anhydrous salt crystallises from hot concentrated solutions on cooling. A tetrahydrate stable at low temperatures is known. One hundred parts of water dissolve (Mulder):—

°C.	Parts $Sr(NO_3)_2$.	°C.	Parts $Sr(NO_3)_2$.
10	54·9	80	97·2
20	70·8	100	101·1
40	91·3	107·9	102·9
60	94·0		

The salt is practically insoluble in strong nitric acid and in absolute alcohol. It is largely used in pyrotechny, and it is generally very pure, containing only traces of calcium and barium.

Analysis. For the estimation of calcium, 10 g. of the salt, dried at 140°, is shaken with 50 c.c. of absolute alcohol for two hours; 50 c.c. of ether is added, the mixture shaken and left to stand twelve hours, and filtered; the residue is washed with ether-alcohol by decantation. The filtrate is evaporated to dryness, the residue dissolved in water, and the calcium precipitated as oxalate.

Barium is separated and estimated as chromate. Two g. is dissolved in 600 c.c. of water. The solution is boiled and treated with 6 drops of acetic acid (sp. gr. 1·065) and 5 c.c. of 10 per cent. ammonium chromate solution. After one hour the precipitate is filtered off, washed with water containing ammonium chromate, then with hot water, and dissolved in 2 c.c. of nitric acid (sp. gr. 1·2). The solution is heated to boiling and reprecipitated with a slight excess of ammonium acetate followed by 2 c.c. of ammonium chromate solution. The precipitate is collected on a Gooch crucible and washed as before, dried, ignited gently, and weighed as $BaCrO_4$.

Estimation of strontium: 0·5 g. is dissolved in water, and the hot solution precipitated with ammonia and ammonium carbonate. The precipitate is filtered off, washed with dilute ammonium carbonate solution, and dissolved in 5 c.c. of hydrochloric acid. The solution is diluted to 300 c.c., heated to boiling, and precipitated by 10 per cent. sulphuric acid added drop by drop from a burette. The precipitate is filtered off, washed with hot water, ignited, and weighed as $SrSO_4 + BaSO_4$. The barium oxide found in the preceding test is then deducted, giving strontium oxide.

Barium Chloride, $BaCl_2+2H_2O$, forms colourless, transparent, rhombic tablets. One hundred parts of water dissolve:—

°C.	Parts $BaCl_2$.	°C.	Parts $BaCl_2$.	°C.	Parts $BaCl_2$.
10	33·3	50	43·6	90	55·6
20	35·7	60	46·4	100	58·8
30	38·2	70	49·4	104·1	60·3
40	40·8	80	52·4		

The solubility decreases in presence of hydrochloric acid; the salt is insoluble in the strong acid and in absolute alcohol. It becomes anhydrous at 113° and melts at 960°.

Barium chloride is used chiefly for the preparation of artificial barium sulphate (*blanc fixe*).

The salt should dissolve in water to a clear solution. One g. in 10 c.c. of water tinted with indigo should show no rapid fading of the blue colour (absence of nitrate) on addition of 5 c.c. of strong sulphuric acid. An aqueous solution of 1 g., precipitated with 10 c.c. of 10 per cent. sulphuric acid and filtered, should give a filtrate yielding less than 0·001 g. of residue on evaporation. No heavy metals should be present (hydrogen sulphide test).

For the determination of barium, 1 g. is dissolved in 300 c.c. of water. The solution, acidified with 3 c.c. of hydrochloric acid, is heated to boiling and precipitated with $N/2$ sulphuric acid added drop by drop from a burette. The precipitate is filtered off next day, washed first with hot dilute hydrochloric acid, then with water, ignited, and weighed as $BaSO_4$.

Barium Nitrate, $Ba(NO_3)_2$, occurs as colourless, transparent, cubic crystals which melt at 593°. One hundred parts of water dissolve:—

°C.	Parts $Ba(NO_3)_2$.	°C.	Parts $Ba(NO_3)_2$.
10	7·0	80	27·0
20	9·2	100	32·2
50	17·1	102	34·8

The solubility is depressed by nitric acid or alcohol, the salt being insoluble in the strong acid and in absolute alcohol. Large quantities of barium nitrate are used in pyrotechny.

The salt should dissolve in water to a clear solution free from any turbidity due to barium sulphate. Chloride should be absent (silver nitrate test). The commercial article sometimes contains iron and

lead, which are detected in the usual manner by means of ammonium sulphide.

Barium Chlorate, $Ba(ClO_3)_2 + H_2O$, crystallises in monoclinic prisms soluble in about three parts of water, and also in alcohol. The salt is used, like the preceding, in pyrotechny. The chief impurity is chloride, which may be present in quantities up to 1 per cent. It is detected and estimated by precipitation with silver nitrate from the solution acidified with nitric acid.

THORIUM AND CERIUM SALTS

Thorium Nitrate, $Th(NO_3)_4 + 12H_2O$. This salt occurs in commerce as granular, crystalline crusts containing on an average 48 per cent. of thoria. The commercial salt does not correspond to a known hydrate but approximates to $Th(NO_3)_4 + 4H_2O$. It is readily soluble in water and in alcohol. On ignition it leaves a white residue of thoria (ThO_2).

Thorium nitrate is largely used in the incandescent mantle industry, for which purpose it must be very pure, and contain not more than traces of heavy metals or iron, not more than 0·004 per cent. of phosphorus, and no detectable traces of cerium and chlorine. The sum of alumina, magnesia, lime, and alkalis should not exceed 0·05 per cent. Twenty-five g. of the salt should dissolve completely in 25 c.c. of cold water to a clear solution showing only the slightest trace of a yellow colour.

Analysis. Sulphuric acid: Commercial thorium nitrate always contains from 0·8 to 1·5 per cent. of SO_3, which is purposely added to ensure the formation of a light, voluminous oxide on ignition. For the estimation of sulphuric acid, 10 g. is dissolved in 250 c.c. of water; 5 c.c. of strong hydrochloric acid is added, followed by 5 g. of pure oxalic acid. The solution is heated on the water-bath until the precipitate becomes granular and settles well, then cooled, and diluted to 500 c.c. Four hundred c.c. is filtered through a dry paper, boiled, and treated drop by drop with 25 c.c. of 10 per cent. barium chloride solution. After standing overnight the precipitate is collected, well washed, dried, ignited, and weighed as $BaSO_4$.

Thoria (residue on ignition): 2 g. is moistened with 4 drops of 25 per cent. ammonia, and heated in a platinum crucible until nitrous fumes are evolved. After cooling a further 4 drops of ammonia are added, and the salt is heated until no further fumes are disengaged. The residue is heated over a blast burner for twenty minutes, cooled, and weighed as ThO_2. Not less than 48 per cent. should be found.

Iron and heavy metals: 20 c.c. of a 30 per cent. solution should give only a slight rose colour with 10 c.c. of 2 per cent. potassium

thiocyanate solution, and only a very slightly darkened liquid with 50 c.c. of saturated hydrogen sulphide water.

Chlorides should be absent, *i.e.* the usual silver nitrate reaction should be negative.

"Didymium": The presence of any appreciable quantity of the two didymium metals reduces the luminosity of the mantle. For a qualitative test, 21 g. of nitrate (approximately 10 g. of thoria) is dissolved in 50 c.c. of water, and 25 c.c. of dilute sulphuric acid (500 g. of the strong acid diluted to 1000 c.c.) is added. After stirring a short time, the bulk of the thoria is precipitated as a crystalline sulphate. The solution contains practically all the didymium, lanthanum, etc., with about 5 per cent. of the thoria. After standing for one hour, the precipitate is sucked dry on the pump and washed with 20 c.c. of 5 per cent. sulphuric acid. The filtrate is treated with a slight excess of ammonia; the precipitated hydroxides are filtered off by suction, washed free from sulphate, and dissolved in 4 c.c. of nitric acid (69 c.c. of strong acid diluted to 250 c.c.). A piece of gas mantle fabric is soaked in this solution, allowed to dry, and burnt in a gas flame free from hydrogen sulphide. The ash should not show any red tinge.

Phosphoric acid: 50 g. of nitrate is dissolved in 125 c.c. of water and 25 c.c. of strong nitric acid. The solution is treated with 125 c.c. of molybdate solution (40 g. ammonium molybdate in 335 c.c. of water and 65 c.c. of 25 per cent. ammonia; the solution is poured into 230 c.c. of nitric acid and 370 c.c. of water) and 50 g. of ammonium nitrate, and allowed to stand overnight on a water-bath. The precipitate is collected, washed with acidulated 15 per cent. ammonium nitrate solution, and dissolved in 15 c.c. of 6 per cent. ammonia. The solution, which should not exceed 40 c.c. in volume, is neutralised with strong hydrochloric acid until the yellow precipitate first formed just redissolves. Ten c.c. of 25 per cent. ammonia and 8 c.c. of magnesia mixture are added, and after standing four hours the precipitate is filtered off, washed with dilute ammonia, ignited and weighed as $Mg_2P_2O_7$.

Cerium is detected by heating a solution of several g. of the salt with ammonia and hydrogen peroxide. No yellow colour should develop in the precipitate.

Alumina, magnesia, lime, alkalis: A solution of 40 g. of nitrate in 150 c.c. of water containing 2 c.c. of nitric acid is precipitated with 19·5 g. of pure oxalic acid. The liquid is diluted to 400 c.c.; 200 c.c. is filtered through a dry paper and evaporated to dryness in a platinum crucible. The residue is ignited and weighed; its weight should not exceed 0·01 g.

The oxalic acid used in the tests should be purified by recrystallisation of the pure commercial acid from strong hydrochloric acid; in any case blank tests must be conducted with the reagents.

Cerium Nitrate, $Ce(NO_3)_3+6H_2O$, occurs as colourless, deliquescent crystals readily soluble in water and in alcohol. It should yield a minimum of 39 per cent. CeO_2 on ignition; the ignited residue should be of a pure light yellow colour.

The salt is added to thorium nitrate so that the thoria in the gas mantle contains 1 per cent. of ceria. The cerium nitrate is analysed in the same way as thorium nitrate.

ALUMINIUM SALTS

Aluminium Sulphate, $Al_2(SO_4)_3+18H_2O$, when pure, contains 15·3 per cent. of alumina; 14·5 per cent. is generally guaranteed in the commercial article, but products richer in alumina (17 to 18 per cent.) are also sold. The pure salt crystallises with difficulty in thin, six-sided plates, very soluble in water: 100 parts of water dissolve at 0°, 86·8 parts, and at 100°, 1132 parts of the hydrated salt. When heated, aluminium sulphate melts in its water of crystallisation and becomes converted into the anhydrous salt. The latter decomposes at a red heat, leaving a residue of alumina.

Aluminium sulphate is largely used in dyeing as a mordant, and for sizing in the manufacture of paper.

Detection of impurities.[1] A *residue* insoluble in water is sometimes obtained; it consists essentially of silica and of very small quantities of alumina and lime, but its amount is generally negligible. *Iron* is the most harmful impurity in dyeing, and only small traces should be present. It is tested for by heating the aluminium sulphate with a little pure nitric acid, adding potassium thiocyanate solution, and extracting with ether, a blank test being carried out with the distilled water and reagents used. 0·001 mg. of iron suffices to impart a distinct rose colour to the ether. With gallic acid solution, traces of iron give a bluish-violet coloration; larger quantities yield a bluish-black ink-like colour. *Copper* is detected by the reddening of a clean piece of iron immersed in the solution. For the detection of *lead* and *zinc*, the solution is treated with pure sodium hydroxide till the precipitate first formed redissolves; any ferric hydroxide is filtered off and the filtrate treated with hydrogen sulphide. If white the precipitate is tested for zinc by solution in hydrochloric acid and precipitation with potassium ferrocyanide; if discoloured, it is also tested for lead by solution in nitric acid and addition of ammonium acetate and potassium dichromate. Zinc is often present, especially in products of French manufacture *Chromium* occurs in some preparations, especially those manufactured from Irish bauxite. According to Marchal and Wiernik,[2] it may be

[1] *Cf.* von Kéler and Lunge, *Z. angew. Chem.*, 1894, 7, 670.
[2] *Z. angew. Chem.*, 1891, 4, 512.

detected by warming the solution with a small quantity of freshly precipitated manganese dioxide, prepared by the interaction of manganous sulphate and potassium permanganate in equimolecular proportions. In presence of even very small quantities of chromium, a distinct yellow coloration is visible in the filtrate, which is turned temporarily blue by hydrogen peroxide. *Arsenic* is found in traces in most commercial samples; for its detection *cf.* p. 397. *Free sulphuric acid* is detected by extracting the thoroughly dried sample with absolute alcohol and testing the solution with litmus paper; a more convenient test is with tincture of logwood made from 1 part of logwood extract, 3 parts of distilled water, and 1 part of alcohol; the violet colour of the tincture is turned to brownish-yellow by free acid. If the quantity of free acid is very small, the quantitative method (*cf.* p. 374) must be used.

Quantitative analysis. This is generally confined to the estimation of alumina; in some cases it is extended to the estimation of iron and of free acid.

Alumina is usually determined gravimetrically by precipitation with ammonia. Blum's method[1] consists in adding ammonium chloride and a slight excess of ammonia, heating the solution till it just boils, and filtering. Lunge[2] found Blum's procedure to be preferable to Fresenius's method, in which the boiling is continued until all the free ammonia has been driven off. Ferric oxide, silica, phosphoric acid, etc., are, of course, precipitated with the alumina; the amount of these in commercial aluminium sulphate is seldom appreciable.

Kretzschmar[3] recommends the phosphate method as being very accurate. Ten g. of the alum or aluminium sulphate is dissolved in water and diluted to 500 c.c.; 50 c.c. of this solution is treated with an excess of sodium phosphate and a little sodium acetate, and the precipitate dissolved in dilute hydrochloric acid. The solution is heated to boiling, a large excess of concentrated sodium thiosulphate solution added, and the mixture boiled until the precipitate settles as soon as the vessel is removed from the wire gauze; longer boiling must be avoided. The precipitate is filtered off, thoroughly washed with hot water, dried, and ignited, finally with free access of air. The weight of the precipitate multiplied by 0·4185 gives the weight of alumina.

The volumetric method is much more rapid. Stock's method[4] is as follows: the salt (aluminium sulphate or alum) is dissolved in water freed from carbon dioxide by boiling. The solution to be titrated, which should not contain more than 0·5 g. of potassium alum per

[1] *Z. anal. Chem.*, 1888, **27**, 19. [2] *Z. angew. Chem.*, 1889, **12**, 635.
[3] *Chem. Zeit.*, 1890, **14**, 1223.
[4] *Ber.* 1900, **33**, 552; see also Kolthoff, *Z. anorg. Chem.*, 1921, **112**, 172; Tingle, *Ind. Eng. Chem.*, 1921, **13**, 420.

100 c.c., is treated with excess of barium chloride (10 c.c. of 10 per cent. solution per g. of alum). The precipitated barium sulphate promotes the settling of the aluminium hydroxide and enables the end-point to be easily observed. The liquid is heated to about 90° and titrated after addition of phenolphthalein, with $N/10$ or $N/5$ sodium hydroxide, solution to the appearance of a faint pink tinge. The standard alkali solution must be free from carbonate, which is ensured by the addition of barium chloride.

Iron. As the amount of iron in aluminium sulphate is small, the colorimetric method of determination with thiocyanate is used; this is given in detail under "Sulphuric Acid" (Vol. I., p. 453). One to two g. of aluminium sulphate is dissolved in a little water, and the solution warmed for a few minutes with 1 c.c. of iron-free nitric acid. The solution is cooled, diluted to 50 c.c., and transferred to the colorimeter cylinder for comparison with the standard iron alum solution.

If it be desired to estimate both ferrous and ferric iron, the total iron is estimated in one portion as described; a second portion is dissolved in air-free, distilled water in an atmosphere of carbon dioxide, and the ferric iron estimated colorimetrically without addition of nitric acid.

Aluminium sulphate for use in turkey-red dyeing should not contain more than 0·001 per cent. of total iron; ferrous salt is less harmful than ferric. The presence of zinc, which, however, seldom occurs, is also injurious to the colour. In dyeing printed woollen goods, on the other hand, iron is not nearly so injurious. In the manufacture of paper, an iron content up to 0·15 per cent. has no effect in sizing good quality writing-paper;[1] while products containing from 0·3 to 0·5 per cent. of iron can be used only for poor quality papers.

Free Acid. The only method to be recommended for technical purposes is that of Beilstein and Grosset.[2] One g. of the sample (or 2 g. in the case of samples poor in acid) is dissolved in 5 c.c. of water; 5 c.c. of a cold, saturated neutral ammonium sulphate solution is added, and the mixture allowed to stand with frequent shaking for a quarter of an hour; it is then precipitated by 50 c.c. of 95 per cent. alcohol, the precipitate filtered off, and washed with 50 c.c. of alcohol. The filtrate is evaporated on the water-bath, the residue taken up with water, and this solution titrated with $N/10$ alkali and phenolphthalein.

Other constituents. Zinc should be estimated whenever present. The simplest method is to add sufficient barium acetate to the solution to precipitate the whole of the sulphuric acid, and then to estimate the zinc in the filtrate as sulphide.

[1] *Papier-Zeit.*, 1891, 2327.

[2] *Z. anal. Chem.*, 1890, **29**, 73. For a recent method not involving the use of alcohol, see Zschokke and Häuselmann, *Chem. Zeit.*, 1922, **46**, 302.

Alums.—The alums of the alkali metals crystallise in colourless regular octahedra. One hundred parts of water dissolve at 16°: hydrated sodium alum, 51 parts; hydrated potassium alum, 15 parts; and hydrated ammonium alum, 12 parts. The examination of these salts is conducted as described above for aluminium sulphate. The estimation of the ammonia and of the alkali is carried out by the ordinary methods.

Sodium Aluminate is used in dyeing, printing, in preparing lakes, and sometimes in sizing paper; also in the manufacture of milk-glass, for hardening bricks, and in soap-making. The analysis is generally limited to the estimation of sodium oxide and of alumina; impurities such as insoluble matter, silica, and iron are sometimes determined.

For the estimation of *sodium oxide* and *alumina*, 20 g. of the salt is dissolved in water and the solution made up to 1000 c.c. Twenty-five c.c. is diluted and treated with carbon dioxide in presence of a little phenolphthalein until the red colour is discharged; the precipitated aluminium hydroxide is filtered off, washed with hot water, ignited, and weighed as alumina. The filtrate is titrated cold with $N/5$ hydrochloric acid after addition of methyl orange, and the number of cubic centimetres used calculated to Na_2O. One c.c. $N/5$ acid $= 0{\cdot}0062$ g. Na_2O.

The *insoluble residue* is estimated in 10 or 20 g. of substance as in the analysis of sodium carbonate (*cf.* Vol. I., p. 558); hardened filter paper should be used for the filtration. *Silica* is estimated by evaporation with hydrochloric acid, filtration, and washing in the usual way. Bayer states[1] that sodium aluminate solution dissolves only a few tenths per cent. of silica, just as conversely water-glass solution can take up only traces of alumina. Traces of *iron* are detected as described on p. 374.

Other Aluminium Salts.—Certain salts (*e.g.* the acetate, thiocyanate chloride, hypochlorite, sulphite, thiosulphate, chlorate) are used as mordants in dyeing and in calico-printing. They are not, as a rule, examined chemically, because the analytical data give the manufacturer but little information as to the practical value of the sample. It is preferable to carry out a practical test, either in dyeing or in printing, and to compare the result with that obtained with a "standard" preparation.

CHROMIUM SALTS

Potassium Chromate, K_2CrO_4 (yellow or neutral chromate of potassium, containing 51·49 per cent. CrO_3). The pure salt crystallises in citron-yellow rhombic pyramids; its aqueous solution reacts slightly alkaline to litmus and neutral to phenolphthalein. It is insoluble in alcohol, and is partially hydrolysed in aqueous solution into potassium

[1] *Z. angew. Chem.*, 1891, 4, 512.

dichromate and potassium hydroxide. It sometimes contains large quantities of the isomorphous potassium sulphate as impurity; the aqueous solution, strongly acidified with hydrochloric acid, then gives a white precipitate with barium chloride. For the quantitative estimation of the sulphate the aqueous solution, acidified slightly with hydrochloric acid, is precipitated with barium chloride, the precipitate washed by decantation and digested with hydrochloric acid and alcohol to dissolve the barium chromate. The content of chromic anhydride is determined by strong acidification of an aqueous solution with sulphuric acid, reduction with an excess of ferrous ammonium sulphate, and titration of the excess of ferrous salt in the very dilute solution with potassium permanganate (*cf.* p. 22).

According to Kremers, Schiff, and Gerlach, the specific gravities of aqueous solutions at 19·5° are as follows:—

Per cent. K_2CrO_4.	Sp. gr.	Per cent. K_2CrO_4.	Sp. gr.	Per cent. K_2CrO_4.	Sp. gr.	Per cent. K_2CrO_4.	Sp. gr.
1	1·008	11	1·093	21	1·186	31	1·292
2	1·016	12	1·101	22	1·196	32	1·304
3	1·024	13	1·110	23	1·207	33	1·315
4	1·033	14	1·120	24	1·217	34	1·327
5	1·041	15	1·129	25	1·227	35	1·339
6	1·049	16	1·138	26	1·238	36	1·351
7	1·058	17	1·147	27	1·249	37	1·363
8	1·066	18	1·157	28	1·259	38	1·375
9	1·075	19	1·167	29	1·270	39	1·387
10	1·084	20	1·177	30	1·281	40	1·399

One hundred parts of water dissolve at:—

°C.	Parts K_2CrO_4 dissolved.	°C.	Parts K_2CrO_4 dissolved.	°C.	Parts K_2CrO_4 dissolved.
0	58 90	40	66·98	80	75·06
10	60·92	50	69·00	90	77·08
20	62·94	60	71·02	100	79·10
30	64·96	70	73·04		

Sodium Chromate, $Na_2CrO_4 + 10H_2O$. This salt, which is very soluble in water, crystallises in yellow needles from a hot solution of sp. gr. 1·563; the crystals are separated from the adhering mother-liquor centrifugally. The salt deliquesces rapidly and liquefies. Alkali sulphate and carbonate are the chief impurities. The content of chromic anhydride is estimated by titration as described above under potassium chromate.

Potassium Dichromate, $K_2Cr_2O_7$ (bichromate of potash, red or acid chromate of potassium, containing 67·98 per cent. CrO_3). The salt comes into commerce as fine orange-red triclinic crystals which are usually contaminated with some potassium sulphate, and which also leave a small insoluble residue on solution in water. It is fusible, like the neutral salt, at a red heat, and at a very high temperature is decomposed into the neutral salt, chromium sesquioxide, and oxygen. The solid salt and its aqueous solution are very poisonous and cauterise strongly. It is insoluble in alcohol.

Potassium dichromate is the source of almost all the other chromium compounds; it is also largely used in dyeing and printing, and as an oxidising agent.

According to Alluard, 100 parts of water dissolve at:—

°C.	Parts $K_2Cr_2O_7$ dissolved.	°C.	Parts $K_2Cr_2O_7$ dissolved.	°C.	Parts $K_2Cr_2O_7$ dissolved.
0	4·6	40	25·9	80	68·6
10	7·4	50	35·0	90	81·1
20	12·4	60	45·0	100	94·1
30	18·4	70	56·7		

The following specific gravities and strengths of solutions at 19·5° are given by Kremers and Gerlach:—

Per cent. $K_2Cr_2O_7$.	Sp. gr.	Per cent. $K_2Cr_2O_7$.	Sp. gr.	Per cent. $K_2Cr_2O_7$.	Sp. gr.
1	1·007	6	1·043	11	1·080
2	1·015	7	1·050	12	1·087
3	1·022	8	1·056	13	1·095
4	1·030	9	1·065	14	1·102
5	1·037	10	1·073	15	1·110

The commercial product is guaranteed to contain from 67·5 to 68·0 per cent. of chromic anhydride; this is determined volumetrically and the sulphuric acid gravimetrically (see potassium chromate, p. 376).

Sodium Dichromate, $Na_2Cr_2O_7$ (containing 76·3 per cent. CrO_3). The pure salt comes on the market as red triclinic prisms which crystallise with two molecules of water; they are very hygroscopic, liquefy easily, melt at just over 100°, and lose their water of crystallisation at this temperature. It is sold in large quantities, however, in a dehydrated condition as a friable mass or in cakes containing sodium sulphate and insoluble carbonaceous matter, etc., as impurities; the content of chromic anhydride should amount to from 73 to 74 per cent.

Pure aqueous solutions have the following specific gravities:[1]—

Per cent. $Na_2Cr_2O_7$.	Sp. gr.	Per cent. $Na_2Cr_2O_7$.	Sp. gr.
1	1·007	30	1·208
5	1·035	35	1·245
10	1·071	40	1·280
15	1·105	45	1·313
20	1·141	50	1·343
25	1·171		

Chromium Fluoride, CrF_3+4H_2O. The fluoride and its double salts are readily dissociated in aqueous solution with separation of chromium hydroxide; they have now been used for some years as mordants in the dyeing industry and in printing. The fluoride comes on the market as a dark green powder, stable in air; it is dissolved in water in wooden or copper vessels.

Chromium acetate, chloride, and sulphate also find extensive application as mordants in dyeing.

Chrome Alum, $K_2SO_4Cr_2(SO_4)_3+24H_2O$ (containing 15·2 per cent. Cr_2O_3, 9·4 per cent. K_2O, 32·1 per cent. SO_3, and 43·3 per cent. H_2O). This salt forms large octahedra, which appear black by reflected, and dark violet by transmitted, light. One hundred parts of water dissolve about 20 parts, producing a bluish-violet coloured solution; on boiling, the solution turns green, and on evaporation, crystals are formed only after the concentrated cold solution has stood for some time. Chrome alum is produced in large quantities as a by-product when a mixture of potassium dichromate and sulphuric acid is used for oxidising purposes, *e.g.*, in the manufacture of anthraquinone.

The content of chromic oxide is determined by oxidation to chromic anhydride, which is titrated. The solution is made alkaline with potassium or sodium hydroxide, small quantities of sodium peroxide added from time to time, the excess of peroxide removed by warming and passing carbon dioxide, the cooled solution then strongly acidified with sulphuric acid, and the chromic anhydride estimated volumetrically as described on p. 376. The presence of potassium sulphate as impurity is ascertained by the usual determination of sulphuric acid, and by the estimation of the loss (water) on moderate ignition.

IRON SALTS

Ferrous Sulphate, $FeSO_4+7H_2O$ (Green Vitriol).—The pure salt forms light bluish-green monoclinic prisms, which quickly effloresce in dry air and become opaque; in moist air the crystals oxidise and

[1] Stanley, *Chem. News*, 1886, **54**, 194. (The temperature at which the specific gravity has been determined is not given.)

gradually become converted into yellowish-brown basic ferric sulphate. It is largely used for the manufacture of ink, iron mordants, and Prussian blue.

Ferrous sulphate is insoluble in alcohol, ether, and concentrated sulphuric acid; the latter separates $FeSO_4 . H_2O$ from concentrated aqueous solutions. One part of the crystallised salt is dissolved by one and a half parts of cold water and one-third part of water at 100°. According to determinations by Gerlach, the specific gravity of pure aqueous solutions of the heptahydrate at 15° is as follows:—

Per cent. $FeSO_4+7H_2O$.	Sp. gr.	Per cent. $FeSO_4+7H_2O$.	Sp. gr.
1	1·005	15	1·082
2	1·011	20	1·112
3	1·016	25	1·143
4	1·021	30	1·174
5	1·027	35	1·206
10	1·054	40	1·239

The content of ferrous iron is determined by titrating a dilute solution, acidified with sulphuric acid, with potassium permanganate (*cf.* Vol. I., p. 59).

Intentional adulteration of the salt is not met with. Ferric sulphate is recognised by addition of potassium thiocyanate to the dilute hydrochloric acid solution. The commercial salt is apt to contain a small admixture of sulphates of copper, zinc, nickel, and manganese. These metals are detected as follows: two or more grams of the salt is dissolved in dilute hydrochloric acid, and the solution treated with hydrogen sulphide. Any precipitate formed is filtered off, washed, and dissolved in nitric acid; addition of excess of ammonia produces a blue colour if copper is present. The filtrate is boiled to expel hydrogen sulphide, oxidised with nitric acid, neutralised with sodium carbonate, and boiled with sodium acetate. The precipitated basic ferric acetate is filtered off and the filtrate divided in two portions. The first is saturated with hydrogen sulphide, which precipitates white zinc sulphide; if the precipitate is discoloured or dark, it must be tested for nickel and zinc by solution in a little *aqua regia* and boiling with sodium hydroxide and bromine water: nickel is detected by the precipitation of black nickelic hydroxide, and zinc by the white sulphide precipitate produced by sodium sulphide in the filtrate from the nickel precipitate. The second portion of the filtrate from the iron precipitate is heated with sodium hydroxide solution and bromine water: a brown precipitate proves manganese to be present. Any nickel contained in the ferrous sulphate would be thrown down as a black

precipitate with the manganic hydroxide, but fusion of the precipitate with sodium carbonate and nitrate on platinum foil produces the characteristic bluish-green manganate melt. Manganese frequently occurs in ferrous sulphate. In order to detect aluminium (the presence of which, for many uses of ferrous sulphate, is specially detrimental) the precipitate of basic ferric acetate is boiled in a platinum dish with pure sodium hydroxide solution (prepared from metallic sodium); the precipitate is filtered off and the filtrate neutralised with acetic acid and boiled, whereby any aluminium present is precipitated.

Ferric Sulphate, $Fe_2(SO_4)_3$+aq. This salt is prepared by the oxidation of a concentrated hot sulphuric acid solution of ferrous sulphate by nitric acid. It usually comes into commerce dissolved as a brown liquid of sp. gr. 1·45 to 1·53, which is used in dyeing; it is also less frequently met with in the solid state as a whitish salt.

For the estimation of the approximate strength of solutions (at 15°) which generally contain free sulphuric acid and some nitric acid as impurities, Wolff has prepared the following table:—

Per cent. $Fe_2(SO_4)_3$.	Sp. gr.	Per cent. $Fe_2(SO_4)_3$.	Sp. gr.
5	1·0426	35	1·3782
10	1·0854	40	1·4506
15	1·1324	45	1·5298
20	1·1825	50	1·6148
25	1·2426	55	1·7050
30	1·3090	60	1·8006

For the accurate estimation of the iron content, a weighed quantity (about 1 g.) of the solution is diluted with water and sulphuric acid, the ferric salt reduced with zinc, and the cooled solution titrated with permanganate. In another small quantity of the solution the sulphuric acid is estimated gravimetrically by Lunge's method (*cf.* Vol. I., p. 367).

The presence of nitric acid in the salt is detected by heating with indigo solution in sulphuric acid, which becomes discoloured. Ferrous sulphate is recognised by the blue coloration given with a solution of potassium ferricyanide, freshly prepared from previously washed crystals, and estimated by direct titration of the diluted, acidified solution with permanganate. Other metals are tested for as described under ferrous sulphate (p. 379).

Iron Alum, $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3+24H_2O$ (Ferric ammonium sulphate). In the pure state, iron alum forms amethyst-coloured octahedra, which dissolve in 3 to 4 parts of cold water. The salt may contain small quantities of ferrous sulphate and of nitric acid from its

preparation (see "Ferric Sulphate," p. 380); in dyeing, it is used in such cases as require a neutral ferric salt.

Ferric Nitrate solution, of a dark reddish-brown colour, is likewise used commercially as an "iron mordant" in dyeing. The strength of pure solutions may be determined by their specific gravity. Franz gives the following data (temperature 17·5°):—

Per cent. $Fe(NO_3)_3$.	Sp. gr.	Per cent. $Fe(NO_3)_3$.	Sp. gr.
5	1·0398	35	1·3164
10	1·0770	45	1·4338
15	1·1182	55	1·5722
25	1·2110	65	1·7532

The liquor generally contains considerable quantities of ferric sulphate. The iron and sulphuric acid are determined by the methods given for ferric sulphate (p. 380). For the estimation of the nitric acid, a weighed small quantity of the mordant is largely diluted with water, boiled with excess of sodium hydroxide, the filtrate from the ferric hydroxide precipitate evaporated, and the nitric acid in this solution converted into ammonia and estimated by Ulsch's or other suitable method (*cf.* Vol. I., p. 476).

Ferrous Acetate, prepared by dissolving iron turnings in crude acetic acid, comes into commerce as a greenish-black solution, which smells strongly of wood-tar, and contains the greater part of the iron as ferrous salt. Usually, only the specific gravity of this black mordant is taken; it should be approximately 1·12 to 1·14.

Ferric Chloride, $FeCl_3$+aq., is sold as a yellow solid mass, approximating to the formula $FeCl_3+6H_2O$, or as a dark brown solution. It is prepared by solution of wrought iron in dilute hydrochloric acid, evaporation of the solution to a sp. gr. of 1·3, and oxidation with nitric acid. By further evaporation of the concentrated solution and cooling, the yellow solid ferric chloride is obtained.

The pure salt must dissolve in water to a clear solution; potassium ferricyanide should not give a blue coloration (ferrous chloride). The filtrate from the precipitation of the hot solution with ammonia should not be coloured blue (copper), and should give no precipitate with ammonium sulphide (copper, zinc, manganese). Free hydrochloric acid is recognised by the white fumes of ammonium chloride formed when a glass rod moistened with ammonia is held close to the surface of the gently warmed concentrated solution; while the blue coloration of zinc iodide-starch paper suspended over the warmed solution indicates free chlorine or nitrous acid. The ferric iron content is best determined

by titration with stannous chloride solution (*cf.* p. 24). Ferrous salt, if present, is estimated by addition of dilute sulphuric acid, phosphoric acid, and manganous sulphate, and titration with permanganate.

The strength of solutions of ferric chloride may be ascertained from the following table, prepared by Franz, giving the sp. gr. at 17·5°:—

Per cent. $FeCl_3$.	Sp. gr.	Per cent. $FeCl_3$.	Sp. gr.	Per cent. $FeCl_3$.	Sp. gr.
2	1·015	22	1·175	42	1·387
4	1·029	24	1·195	44	1·412
6	1·044	26	1·216	46	1·437
8	1·058	28	1·237	48	1·462
10	1·073	30	1·257	50	1·487
12	1·086	32	1·278	52	1·515
14	1·105	34	1·299	54	1·544
16	1·122	36	1·320	56	1·573
18	1·138	38	1·341	58	1·602
20	1·154	40	1·362	60	1·632

For the examination of *Potassium Ferrocyanide* (yellow prussiate of potash), *cf.* Vol. I., p. 630; *Potassium Ferricyanide* (red prussiate of potash), *cf.* Vol. I., p. 639; *Sodium Ferrocyanide*, *cf.* Vol. I., p. 630.

MANGANESE SALTS

Potassium Permanganate, $KMnO_4$. The pure salt crystallises in dark red rhombic needles, with a greenish metallic lustre; it dissolves in 15 parts of cold and in 2 parts of hot water. A product specially prepared for disinfection purposes comes into commerce as a green or dark red crumbly mass which contains potassium or sodium manganate and permanganate, oxides of manganese, free alkali, potassium and sodium nitrate, potassium chlorate, and potassium chloride.

The solution, acidified with sulphuric acid, is completely decolorised on warming with a little oxalic acid, and also on addition of an aqueous solution of sulphur dioxide; with excess of ammonia and some ammonium sulphide, the colourless solution gives a flesh-coloured precipitate of manganese sulphide. When potassium permanganate is warmed with dilute sulphuric acid, any chlorine present (as chloride and chlorate) will be evolved, and is most easily recognised by means of potassium iodide-starch paper.

The pure salt should be tested for sulphate. The solution is

boiled with a large quantity of pure hydrochloric acid; the acid is nearly neutralised with ammonia, and the hot solution precipitated with barium chloride. For the estimation of chlorides the solution is decolorised by warming with alcohol and nitric acid, and precipitated with silver nitrate. The amount of permanganate contained in the purer products is determined volumetrically with standard acid ferrous sulphate, added to the very dilute solution.

Sodium Permanganate, $NaMnO_4$. This salt is very soluble in water, has no tendency to crystallise, and comes on the market as a solid crumbly mass and in concentrated solutions. Both products are very impure (*cf.* above, "Potassium Permanganate.")

Manganous Sulphate, Chloride, and Acetate find limited application in dyeing for the preparation of manganese bistre. The salts used for this purpose must be free from iron, which is readily verified by warming the solution with a little nitric acid and adding potassium thiocyanate solution. A small amount of calcium, which is always present, is innocuous.

ZINC SALTS

Zinc Sulphate, $ZnSO_4 + 7H_2O$. In the pure state this salt forms colourless, rhombic crystals having a vitreous lustre, which rapidly effloresce in dry air, and dissolve in their water of crystallisation when quickly heated. It crystallises from solution at 30° with 6 molecules of water. When the salt is heated to a little over 100°, it loses 6 molecules of water, whilst the last molecule is driven off only by gentle ignition. On strong ignition, it is decomposed into zinc oxide, sulphur dioxide, and oxygen.

The crude salt comes on the market in cakes, or in the form of cones prepared by fusion of the crystals. The most frequent impurity is manganous sulphate; less frequently, small quantities of the sulphates of copper, cadmium, iron, calcium, and magnesium may be present. Manganese and iron are separated by addition of excess of ammonia to the aqueous solution of the salt; on standing with access of air, both are precipitated as hydroxides. Manganese may also be detected by the appearance of a purple tint when the solution is heated with nitric acid and lead peroxide. Copper and cadmium are precipitated by hydrogen sulphide from the aqueous solution slightly acidified with sulphuric acid. The negligible impurities of calcium and magnesium sulphates do not interfere in any way with the technical uses of the salt (chiefly in the manufacture of lithopone, also in dyeing).

One hundred parts of water dissolve at:—

°C.	Parts.		°C.	Parts.	
	$ZnSO_4$ dissolved.	$ZnSO_4+7H_2O$ dissolved.		$ZnSO_4$ dissolved.	$ZnSO_4+7H_2O$ dissolved.
0	43·02	115·22	60	74·20	313·48
10	48·36	138·21	70	79·25	369·36
20	53·13	161·49	80	84·60	442·62
30	58·40	190·90	90	89·78	533·02
40	63·52	224·05	100	95·03	653·59
50	68·75	263·84			

The specific gravity of solutions at 15° is as follows:—

Per cent. $ZnSO_4+7H_2O$.	Sp. gr.	Per cent. $ZnSO_4+7H_2O$.	Sp. gr.
5	1·029	35	1·231
10	1·059	40	1·271
15	1·091	45	1·310
20	1·124	50	1·352
25	1·167	55	1·399
30	1·193	60	1·445

Zinc Chloride, $ZnCl_2$. The anhydrous chloride is a transparent white mass of sp. gr. 2·75 (butter of zinc), which is very hygroscopic, very soluble in water and in alcohol, melts at 100°, and distils at a red heat. It withdraws the elements of water from organic substances and carbonises wood; its concentrated aqueous solution converts paper into parchment paper and acts as a powerful caustic. It comes into commerce in sticks, which are generally tested only for their solubility in water (freedom from oxychloride). The concentrated aqueous solutions of zinc chloride, which are also commercial products, are tested for free acid (decolorisation of ultramarine paper), sulphate, and specific gravity.

According to Krämer, the specific gravity of aqueous solutions at 19·5° is as follows:—

Per cent. $ZnCl_2$.	Sp. gr.	Per cent. $ZnCl_2$.	Sp. gr.
5	1·045	35	1·352
10	1·091	40	1·420
15	1·137	45	1·488
20	1·186	50	1·566
25	1·238	55	1·650
30	1·291	60	1·740

Zinc Acetate, $Zn(C_2H_3O_2)_2+2H_2O$, is very readily soluble in water, and is used as a mordant in dyeing. It is tested for impurities in the same way as zinc sulphate.

NICKEL SALTS

Nickel Sulphate, $NiSO_4+7H_2O$, crystallises in green rhombic prisms which become anhydrous above 280°. One hundred parts of water dissolve, according to Mulder :—

°C.	Parts $NiSO_4$.	°C.	Parts $NiSO_4$.	°C.	Parts $NiSO_4$.
0	29·3	40	49·0	80	71·7
10	34·0	50	54·5	90	77·6
20	39·0	60	60·2	100	83·7
30	44·0	70	65·9	108·4	88·7

One hundred parts of saturated solution contain (Steele and Johnson) :—

°C.	Parts $NiSO_4$.	°C.	Parts $NiSO_4$.
0	21·4	50	33·4
15	25·5	60	35·4
30	29·8	80	38·7
44·7	32·4	99	43·4

The salt is used in the preparation of the contact mass for the catalytic hydrogenation of oils, and in nickel-plating.

Analysis. Fifty g. is dissolved in distilled water and the solution filtered into a graduated 1000 c.c. flask. The insoluble residue is ignited and weighed; the filtrate is made up to bulk and used for the determination of the following impurities :—

(*a*) Iron. Two hundred c.c. is boiled with a little nitric acid and treated with ammonia in excess. The precipitate is collected and dissolved in hydrochloric acid, the solution reprecipitated with ammonia, and the precipitate filtered off, washed, ignited, and weighed as Fe_2O_3.

(*b*) Manganese. The combined filtrates from the iron precipitation are digested hot, for some time, with bromine water. The precipitate is collected on a filter and well washed till free from chloride. It is dissolved in sulphuric acid and a little hydrogen peroxide. After

the excess of the latter has been destroyed by boiling, the solution is boiled with silver nitrate and ammonium persulphate; the permanganic acid thus formed is titrated with sodium arsenite or estimated colorimetrically.

(*c*) Copper. Two hundred c.c. is acidified with 30 c.c. of hydrochloric acid and saturated with hydrogen sulphide. The precipitate is filtered off, well washed with acidulated hydrogen sulphide water, and dissolved in nitric acid; the copper in the solution is estimated colorimetrically.

(*d*) Cobalt. Two hundred c.c. is treated with 10 c.c. of strong hydrochloric acid, heated to boiling, and precipitated by addition of 50 c.c. of a solution containing 8 g. of nitroso-β-naphthol in 300 c.c. of glacial acetic acid and 300 c.c. of water. The precipitate is collected next day, washed with 12 per cent. solution of hydrochloric acid, then with water, ignited with 2 g. of oxalic acid, and weighed as Co_3O_4, or it may be reduced to metal in a current of hydrogen. If copper or iron is present the ignited oxide is dissolved in hydrochloric acid and the copper removed with hydrogen sulphide. The filtrate is oxidised with nitric acid and the iron eliminated by double or treble precipitation with ammonia. The cobalt in the combined filtrates is precipitated with yellow ammonium sulphide; the precipitate is filtered off and ignited, converted into sulphate by gentle heating with a drop of strong sulphuric acid, and weighed as $CoSO_4$.

Nickel is estimated, if desired, in 10 c.c. of filtrate by titration with cyanide (see p. 68).

Nickel Ammonium Sulphate, $NiSO_4 \cdot (NH_4)_2SO_4 + 6H_2O$. This compound, also known as "double salt" (nickel sulphate being the "single salt"), is used, on account of its greater purity, in nickel-plating. It crystallises in green, short monoclinic prisms. One hundred parts of water dissolve the following quantities (Link):—

°C.	Parts $NiSO_4 \cdot (NH_4)_2SO_4$.	°C.	Parts $NiSO_4 \cdot (NH_4)_2SO_4$.
3·5	1·8	40	11·5
16	5·8	50	14·4
20	5·9	68	18·8
30	8·3	85	28·6

The salt is almost insoluble in a strong solution of ammonium sulphate acidified with sulphuric acid.

The analysis is carried out as described above for nickel sulphate.

COPPER SALTS

Copper Sulphate, $CuSO_4+5H_2O$ (*Blue Vitriol*). The salt comes on the market as large, bright blue, transparent triclinic crystals, which effloresce superficially in dry air. As impurities it most frequently contains ferrous sulphate, less frequently considerable quantities of zinc and nickel sulphates; it invariably contains traces of bismuth, arsenic, and antimony. Usually only iron is tested for by saturating an aqueous solution with ammonia, filtering through a white paper, washing first with ammonia and then with water; on drying small traces of iron hydroxide are easily visible. Sulphuric acid and combined water are estimated in separate portions by the usual methods; a third portion is dissolved in dilute hydrochloric acid, and the copper precipitated with hydrogen sulphide; the filtrate is oxidised with potassium chlorate, and the iron precipitated as basic acetate. In the filtrate from the iron, zinc and nickel are precipitated by boiling with sodium carbonate. For an accurate analysis, Hampe's method for the Analysis of Commercial Copper (pp. 199 *et seq.*) is recommended. The copper content is most conveniently estimated by electrolysis. If the copper is separated electrolytically from 3 to 5 g. of the salt, the presence of appreciable quantities of arsenic and antimony can be recognised (*cf.* p. 194).

On being heated to about 200°, copper sulphate loses all its water of crystallisation and yields a white, very hygroscopic powder, insoluble in alcohol. According to Poggiale, 100 parts of water dissolve:—

at	10°	20°	40°	80°	100°	
	36·9	42·3	56·9	118·0	203·3	parts $CuSO_4+5H_2O$.
	20·9	23·5	30·3	53·1	75·3	„ $CuSO_4$.

The specific gravity of solutions at 15° is as follows:—

Per cent. $CuSO_4+5H_2O$.	Sp. gr.	Per cent. $CuSO_4+5H_2O$.	Sp. gr.	Per cent. $CuSO_4+5H_2O$.	Sp. gr.
1	1·007	10	1·069	19	1·144
2	1·013	11	1·076	20	1·152
3	1·020	12	1·084	21	1·160
4	1·027	13	1·091	22	1·169
5	1·033	14	1·096	23	1·177
6	1·040	15	1·114	24	1·185
7	1·048	16	1·121	25	1·193
8	1·055	17	1·129		
9	1·062	18	1·137		

Cupric Chloride, $CuCl_2+2H_2O$. This salt is generally only tested for the presence of iron, as described above for copper sulphate, and the content of copper determined either by titration of the hot

hydrochloric acid solution with stannous chloride or by means of the iodide method (pp. 182 *et seq.*). Salts of the alkalis (sodium chloride, etc.) present as impurities are detected by precipitation of the aqueous solution of the salt with hydrogen sulphide and evaporation of the filtrate from the copper sulphide. The pure hydrated salt forms beautiful green rhombic prisms or needles. The anhydrous chloride, obtained when the hydrated salt is heated above 100°, forms a brown, very hygroscopic mass; it is readily soluble both in water and alcohol.

According to Franz, aqueous solutions at 17·5° have the following specific gravities:—

Per cent. $CuCl_2$.	Sp. gr.	Per cent. $CuCl_2$.	Sp. gr.	Per cent. $CuCl_2$.	Sp. gr.
2	1·018	16	1·170	30	1·362
4	1·036	18	1·195	32	1·395
6	1·055	20	1·222	34	1·429
8	1·073	22	1·250	36	1·462
10	1·092	24	1·278	38	1·495
12	1·118	26	1·306	40	1·528
14	1·144	28	1·334		

Copper Nitrate, $Cu(NO_3)_2+6H_2O$. The hexahydrate, obtained at a low temperature, melts at about 30°, and forms light blue tabular crystals; at a slightly higher temperature, dark blue prismatic crystals of the trihydrate are obtained, which melt at 115°. Both salts are readily soluble in water and in alcohol, and are very hygroscopic.

The following substances occur as impurities:—nitrates of lead, zinc, and sodium, and sulphates of copper and sodium. The commercial product, not intentionally adulterated, may contain up to 7 per cent. of impurities.

Lead may be separated and estimated as sulphate by evaporation of the solution with excess of sulphuric acid; the copper is deposited electrolytically in the filtrate from the lead sulphate, and, in the solution freed from copper, the zinc is precipitated as sulphide after neutralisation with ammonia. The filtrate from the zinc sulphide is evaporated, the ammonium salts driven off, and the calcium, magnesium, and alkali salts determined in the ignited residue. For the estimation of the sulphuric acid, a separate portion is repeatedly evaporated with hydrochloric acid, and the diluted hot hydrochloric acid solution precipitated with barium chloride.

Copper Acetate, $Cu(C_2H_3O_2)_2+H_2O$ (*Crystallised Verdigris*). The dark bluish-green crystals which come on the market are generally very pure and contain only an extremely small quantity of iron as impurity. The salt is tested for purity in the same way as copper sulphate.

LEAD SALTS

Lead Acetate, $Pb(C_2H_3O_2)_2+3H_2O$ (*Sugar of Lead*). The pure salt crystallises in colourless plates or columns which effloresce in dry air, gradually losing water and some acetic acid and taking up carbon dioxide. The freshly prepared salt dissolves completely in water to a clear solution; the solution of the effloresced salt is milky owing to the presence of lead carbonate, which dissolves on addition of a few drops of acetic acid. At 75° the salt melts, at 100° it becomes anhydrous and solid, and again melts at 280°. One part of the salt dissolves in one and a half parts of water at 15°, in one part at 40°, and in one-half part at 100°. Alcohol dissolves about one-eighth of its weight; it is insoluble in ether. If the solution is precipitated with hydrogen sulphide, the filtrate from the lead sulphide should leave no residue on evaporation (iron). Copper is tested for by precipitation of a concentrated aqueous solution of the salt with sulphuric acid and addition of excess of ammonia to the evaporated filtrate from the lead sulphate.

Brown sugar of lead, prepared from crude pyroligneous acid and litharge, comes on the market in a fused condition as irregular lumps. The content of lead is estimated by precipitation of the solution with sulphuric acid.

Salomon estimates the content of acetic acid in lead acetate by making the solution strongly alkaline with standard potassium hydroxide solution in presence of phenolphthalein, and titrating back the excess with a standard solution of acetic acid of equivalent strength till the red colour disappears. The difference gives the acetic acid in combination with the lead. Lead vinegar is first acidified with standard acetic acid, excess of potassium hydroxide solution then added, and the excess titrated back with acetic acid.

Fresenius mixes an aqueous solution of 5 g. of lead acetate in a 250 c.c. flask with a measured small excess of standard sulphuric acid, fills up to the mark, adds an amount of water equal to the volume of the precipitated lead sulphate (sp. gr. 6·3), shakes, and filters through a dry filter paper. The sulphuric acid in 50 c.c. of the filtrate is precipitated with barium chloride, the barium sulphate weighed, and the content of lead in the acetate calculated from the sulphuric acid used for the precipitation of the lead. Further portions of 50 c.c. are titrated with normal alkali, the sulphuric acid deducted, and the content of acetic acid in the lead acetate thereby ascertained.

Lead Nitrate, $Pb(NO_3)_2$. The salt comes into commerce as colourless or white regular crystals (octahedra and cubo-octahedra), which seldom contain any appreciable quantity of impurities. It is fairly soluble in water; a solution saturated at 20° (sp. gr. 1·415) contains 37 per cent. of lead nitrate. Dilute nitric acid and 90 per cent. alcohol

dissolve it but very slightly; it is insoluble in strong nitric acid and in absolute alcohol.

For the examination of the salt, the lead is converted into sulphate by evaporation of the solution with excess of sulphuric acid; any residue obtained by evaporation of the filtrate from the lead sulphate is examined for copper, iron, and calcium.

Lead Sulphate, $PbSO_4$. Crude lead sulphate is obtained in large quantities as a by-product in the preparation of aluminium acetate and ferric acetate solutions for calico-printing, and is chiefly bought up by lead works. Smaller quantities are worked up into lead colours (white lead, chrome yellow, red lead). It comes on the market as a brown-coloured mass containing water; the colour arises from the lead-vinegar used for the decomposition of the alum or iron alum. The examination is usually limited to the determination of lead. An average sample of several grams is dissolved in a hot concentrated solution of ammonium acetate, the solution filtered, and pure lead sulphate precipitated from the filtrate by addition of excess of sulphuric acid. In lead works the product is assayed in the dry way, by fusion with potassium carbonate, argol, and iron (*cf.* " Assay of Lead," pp. 225 *et seq.*).

TIN SALTS

Stannous Chloride, $SnCl_2+2H_2O$ (*Tin Salt*). The commercial product consists of colourless or pale yellowish-white crystals possessing a fatty appearance, which are freed from the adhering mother-liquor centrifugally. It usually contains, in small quantities, only the impurities arising from the tin and hydrochloric acid used in its preparation; it is seldom adulterated with magnesium or zinc sulphates.

The salt only dissolves completely in a little water and in absolute alcohol when freshly prepared. If it is exposed to the air for any length of time, the oxychloride is formed, which is insoluble in water; on being heated with hydrochloric acid and tin, this is again converted into stannous chloride. When an aqueous solution of the salt is largely diluted, considerable separation of the oxychloride, Sn(OH)Cl, takes place; solutions containing hydrochloric acid, ammonium chloride, or tartaric acid, remain clear. The solid salt and its solutions rapidly absorb oxygen from the air.

The content of stannous chloride is estimated by iodine or ferric chloride titration (*cf.* pp. 260 *et seq.*). For the determination of total tin, the hydrochloric acid solution is reduced with pure zinc or aluminium; the metallic sponge is dissolved in hydrochloric acid in an atmosphere of carbon dioxide, and the solution titrated as before.

The presence of lead, copper, zinc, and iron, as impurities, is detected by addition of excess of ammonia to a solution of the salt, and digestion

on a steam-bath for some time with a considerable quantity of yellow ammonium sulphide, when the above metals remain undissolved as sulphides. Sulphates produce a precipitate of barium sulphate in a largely diluted hydrochloric acid solution. According to Merz, zinc and magnesium sulphates remain undissolved as minute crystals, if several grams of the salt are stirred with five times their weight of absolute alcohol; any tin oxychloride which may be present remains undissolved as a flocculent residue.

The strength of aqueous solutions containing hydrochloric acid may be approximately estimated from their specific gravity. Gerlach has drawn up the following table for solutions at 15°:—

Per cent. $SnCl_2+2H_2O$.	Sp. gr.	Per cent. $SnCl_2+2H_2O$.	Sp. gr.	Per cent. $SnCl_2+2H_2O$.	Sp. gr.	Per cent. $SnCl_2+2H_2O$.	Sp. gr.
2	1·013	22	1·161	42	1·352	62	1·613
4	1·026	24	1·177	44	1·374	64	1·644
6	1·040	26	1·194	46	1·397	66	1·677
8	1·054	28	1·212	48	1·421	68	1·711
10	0·068	30	1·230	50	1·445	70	1·745
12	1·083	32	1·249	52	1·471	72	1·783
14	1·097	34	1·268	54	1·497	74	1·821
16	1·113	36	1·288	56	1·525	75	1·840
18	1·128	38	1·309	58	1·554		
20	1·144	40	1·330	60	1·582		

Stannic Chloride, $SnCl_4$. The pure liquid compound finds its way but seldom into commerce; it occurs much more frequently as a hydrated salt-like mass containing sodium chloride, and as concentrated solutions. In the dyeing industry, solutions of tin in aqua regia are called tin nitrate, tin composition, tin solution, physic, scarlet composition, rosing salt, etc., and are usually contaminated with free nitric acid, ferric chloride, zinc chloride, salt, and stannous chloride, or contain, in the case of the three latter products, intentional additions of such salts. The chloride forms a pentahydrate, and this white salt is used for the same purposes as the other preparations.

The presence of stannous chloride is recognised by the separation of mercurous chloride on the addition of a solution of mercuric chloride; copper, lead, zinc, and iron remain as insoluble sulphides on treatment with ammonia and ammonium sulphide (*cf.* under stannous chloride). Salts of the alkalis, together with zinc and iron salts, are detected by evaporation of the filtrate from the precipitation of the tin by hydrogen sulphide. The presence of nitric acid is shown by the addition of a crystal of ferrous sulphate, when the liquid surrounding the crystal is coloured red.

The total content of tin is determined by precipitation with excess of pure zinc; the precipitated tin is filtered off, dissolved in hydrochloric

acid in a current of carbon dioxide, and titrated with iodine or ferric chloride. The stannous chloride is titrated in a separate sample by means of iodine, stannic chloride being found by difference.

If the solution of stannic chloride does not contain too much impurity, its strength may be estimated approximately from its specific gravity. For this purpose the following table by Gerlach for a temperature of 15° may be employed:—

Per cent. $SnCl_4 . 5H_2O$.	Sp. gr.	Per cent. $SnCl_4 . 5H_2O$.	Sp. gr.
5	1·030	45	1·320
10	1·059	50	1·366
15	1·091	55	1·416
20	1·124	60	1·468
25	1·158	65	1·526
30	1·195	70	1·587
35	1·235	80	1·727
40	1·276	90	1·893

Tin Ammonium Chloride, $SnCl_4 . 2NH_4Cl$ (*Pink Salt*). This salt forms beautiful white crystals, which dissolve readily in water. The content of tin is estimated as above (under Stannic Chloride), since the salt frequently contains an excess of ammonium chloride. It is much used in dyeing as a substitute for the more strongly corrosive stannic chloride.

Sodium Stannate, $Na_2SnO_3 + 3H_2O$ (*Preparing Salts*). The pure salt forms colourless crystals; the ordinary commercial product is usually largely contaminated with sodium carbonate and hydroxide, and not infrequently also contains arsenic. For the estimation of tin, the salt is dissolved in water, the solution treated with excess of hydrochloric acid, and the tin precipitated with pure zinc; the precipitate is dissolved in hydrochloric acid, air being excluded, and the solution titrated, as described for stannic chloride. Arsenic is tested for in a simple Marsh apparatus.

BISMUTH AND ANTIMONY SALTS

Bismuth Nitrate, $Bi(NO_3)_3 + 5H_2O$, crystallises in transparent triclinic prisms which are very deliquescent. The salt is decomposed by water with formation of the basic nitrate, but is completely soluble in dilute nitric acid containing 83 g. of acid per litre. The solution corrodes filter paper. If one part of the salt is treated with 50,000 parts of water, no bismuth is found in solution. On ignition, bismuth nitrate eventually leaves a residue of oxide.

The salt is used for the manufacture of the subnitrate, carbonate, and other bismuth preparations. It is tested as explained under bismuth subnitrate.

Basic Bismuth Nitrate (*Bismuth Subnitrate*) is a white microcrystalline powder. It approximates to the formula $Bi(OH)_2NO_3$, but its composition varies slightly according to the amount of water used in its preparation. It is insoluble in, and slowly decomposed by, water, with loss of nitric acid: on moistening, it reddens blue litmus paper.

Bismuth subnitrate is used in medicine, as a cosmetic, and in the production of iridescent glazes on porcelain. The medicinal product is a heavy white powder, odourless and tasteless, completely soluble in hydrochloric or nitric acid. Commercial varieties may contain silver, lead, copper, arsenic, and ammonium salts. Small quantities of chloride, sulphate, selenium, and tellurium may also be present.

For the detection of impurities, 3 g. is dissolved in 4 c.c. of nitric acid, and the solution poured into 100 c.c. of water. The precipitate is filtered off, the filtrate concentrated to 30 c.c., again filtered, and the solution divided in four portions. These are tested as follows: (*a*) Lead. Five c.c. of dilute sulphuric acid should give no turbidity after fifteen minutes. (*b*) Copper. Excess of ammonia should produce no blue colour. (*c*) Silver. Dilute hydrochloric acid should not cause any cloudiness. (*d*) Sulphate. Barium chloride solution should produce no precipitate.

Arsenic is tested for by ignition of 1 g., which should leave a residue of 0·79 to 0·82 g. This is dissolved in hot sulphuric acid, and the solution is tested in the Marsh-Berzelius apparatus; no mirror should be produced. According to the British Pharmacopœia, not more than two parts of arsenic per million should be present (see Appendix, p. 398).

Selenium and tellurium: 1 g. is dissolved in 1·5 c.c. of nitric acid; 10 c.c. of 10 per cent. ammonium chloride solution is added, and the liquid is diluted to 100 c.c. The precipitate of bismuth oxychloride is filtered off and the filtrate treated with 10 g. of sodium sulphite. No red or black coloration or precipitate should be produced after twelve hours' standing.

Analysis. If no fixed impurities are present, 1 g. of the salt is ignited gently to dull redness, and the residue weighed as Bi_2O_3 (79 to 82 per cent.). In presence of non-volatile impurities, bismuth is conveniently estimated as phosphate according to the method of Schoeller and Waterhouse.[1] 0·5 g. is dissolved in very little nitric acid; the solution is diluted to about 70 c.c. and carefully treated with ammonia until a slight permanent precipitate is obtained. This is redissolved in 2 c.c. of strong nitric acid, the clear liquid heated to boiling,

[1] *Analyst*, 1920, **45**, 435; see also Luff, *Chem. Zeit.*, 1923, **47**, 133.

and precipitated whilst boiling with 50 to 60 c.c. of 10 per cent. di-ammonium phosphate solution contained in a burette. The addition should at first be made drop by drop; once the bismuth phosphate is thrown down, the remainder of the precipitant may be added more rapidly. The solution should be kept stirred to prevent bumping. It is next diluted to 400 c.c. with boiling water and left to settle; the precipitate is filtered off, washed with 3 per cent. ammonium nitrate solution, dried, ignited, and weighed as $BiPO_4$.

Bismuth Carbonate is a heavy white powder insoluble in water, soluble in hydrochloric or nitric acid. Its composition is approximately $2(BiO)_2CO_3 + H_2O$. It loses water at 100° and is converted into oxide on ignition. Its chief use is in medicine. It is examined in the same way as the subnitrate (p. 393).

Potassium Antimonyl Tartrate, $2K(SbO)C_4H_4O_6 + H_2O$ (*Tartar Emetic*), forms colourless efflorescent rhombic prisms soluble in 3 parts of hot and 15 parts of cold water.

The salt is used in medicine and as a mordant in dyeing and printing. It occurs in commerce as white crystals or powder; the technical grades often contain distinct traces of arsenic, which may be detected by the Bettendorf test. Excess of potassium bitartrate may also be present; this is recognised by effervescence due to liberation of carbon dioxide when the solution is treated with sodium bicarbonate solution. Certain mordanting mixtures have been found to contain considerable amounts of zinc sulphate. For the detection of zinc, 1 g. is dissolved in water containing 2 g. of tartaric acid; the solution is made alkaline with potassium hydroxide and saturated with hydrogen sulphide. A white amorphous precipitate proves zinc to be present. Sulphate is detected as usual by addition of barium chloride to the solution acidified with hydrochloric acid.

For the estimation of antimony, 0·5 g. is dissolved in water together with 5 g. of Rochelle salt and 1·5 g. of sodium bicarbonate; the solution is titrated with $N/10$ iodine solution and starch. Alternatively, 0·5 g. of the salt is dissolved in 20 c.c. of water and 20 c.c. of strong hydrochloric acid; 80 c.c. of water is added, and the cold solution titrated with $N/10$ permanganate.

The medicinal salt should be free from lead, copper, iron, sodium, ammonium, chloride, and sulphate. No arsenic limit is given by the British Pharmacopœia.

On account of the high price of tartar emetic, several cheaper antimony salts are now being used as mordants. The two most important are; antimony potassium oxalate, $Sb(C_2O_4K)_3 + 6H_2O$, soluble in water without decomposition; and the double salt $SbF_3 . (NH_4)_2SO_4$. This has to be stored and used in wooden vessels.

MERCURY SALTS

Mercuric Chloride, $HgCl_2$ (*Corrosive Sublimate*), crystallises in rhombic needles, but usually occurs in commerce as semi-transparent crystalline crusts. One hundred parts of water dissolve (Poggiale):—

at	10°	20°	50°	80°	100°
	6·57	7·39	11·34	24·3	53·96 parts $HgCl_2$.

It dissolves in 3 parts of alcohol and in 4 parts of ether. The pure salt melts at 288° and boils at 303°; it can readily be sublimed. Its chief use is as an anti-putrescent for dressing furs and skins and as a disinfectant in medicine.

A frequent impurity of corrosive sublimate is mercurous chloride; this is detected by its insolubility in water, alcohol, and ether. The aqueous solution, after precipitation with hydrogen sulphide and filtration, should leave no residue (or less than 0·2 per cent.) upon evaporation. Two g. of the salt, on heating in a dry clean test tube, should leave no fixed residue.

For the determination of mercury, 0·5 g. dissolved in 20 c.c. of water is heated on a steam-bath with 10 c.c. of hypophosphorous acid until the precipitated mercury collects into a globule. The metal is poured upon a filter paper, washed with water, alcohol, and ether, dried over sulphuric acid, and weighed. Stannous chloride solution may be used instead of hypophosphorous acid; enough should be added to the acidified solution to convert the white precipitate first formed into a grey one of metallic mercury; the washing is done at first with dilute hydrochloric acid.

Mercurous Chloride, $HgCl$ (*Calomel*), is prepared by sublimation of a mixture of mercury and mercuric chloride; the excess of the latter is removed by washing with water.

It forms a white, crystalline, insoluble powder which sublimes without fusion at a red heat. It is used in medicine.

The commercial article sometimes contains mercuric chloride which is readily removed by washing with water or hot alcohol. One g. of calomel, shaken with 10 c.c. of water, should give a filtrate in which neither hydrogen sulphide nor silver nitrate produce any turbidity. 0·5 g. should leave no appreciable residue on gentle ignition.

Mercurous Nitrate, $HgNO_3 + H_2O$. Transparent monoclinic efflorescent prisms, completely soluble in little water, but decomposed by much water with formation of insoluble, white to yellowish, basic salts. Dilute nitric acid furnishes a clear solution which stains the skin and is precipitated by hydrochloric acid.

The salt should be colourless, or show no more than a faint yellowish tinge. One g. should give a clear solution in 1 c.c. of water and 3 drops of 25 per cent. nitric acid (freedom from basic salt). One g. of the salt, triturated with 1 g. of sodium chloride and a little water, should give a paste free from any grey or yellow tinge, and a filtrate which remains clear on treatment with stannous chloride or hydrogen sulphide (absence of mercuric nitrate). The mercury is estimated as described under "Mercuric Chloride" (p. 395).

SILVER AND GOLD SALTS

Silver Nitrate, $AgNO_3$ (*Lunar Caustic*). The pure salt crystallises in large colourless rhombic plates, which, in presence of dust, blacken in the light. At 218° the nitrate melts and solidifies to a crystalline, radiating mass on cooling. It is readily soluble in water and in alcohol. One hundred parts of water dissolve;—

at	0°	19·5°	54°	85°	100°	
	121·9	227·3	500	714	1111	parts of $AgNO_3$.

The pure salt dissolves to a perfectly clear solution in water; the colourless solution should not become turbid (lead, bismuth) or blue (copper) on the addition of a large excess of ammonia.

The content of silver is determined gravimetrically as silver chloride or volumetrically by titration with ammonium thiocyanate according to Volhard's method (p. 122). The salt, as it comes on the market in the form of sticks for surgical purposes, cannot be distinguished in appearance from that fused with potassium nitrate, which is prepared for the same use. The content of nitre is either calculated by difference from the result of the silver determination, or the filtrate from the silver chloride is evaporated with hydrochloric acid and the residual potassium chloride calculated to potassium nitrate. For the detection of potassium nitrate, a strip of filter paper is moistened with the aqueous solution, dried, and ignited; potash is indicated by the strongly alkaline reaction of the ash.

Chlorauric Acid, $HAuCl_4+4H_2O$, crystallises in long yellow needles. By careful ignition in a covered porcelain crucible to a bright red heat, it leaves a residue of pure gold (47·85 per cent.).

Sodium Chloraurate, $NaAuCl_4+2H_2O$ (*Gold Salt*), is much used in photography. It crystallises in yellowish-red rhombic prisms, which are very soluble in water. The percentage of gold is 49·5.

Potassium Chloraurate, $KAuCl_4+2H_2O$, and **Ammonium Chloraurate,** $2NH_4AuCl_4+5H_2O$, are yellow salts which crystallise well and are used for the same purposes as "gold salt."

For the estimation of the gold, a weighed amount of the salt is mixed with half its weight of sodium carbonate, and gradually heated to a dull red heat in a covered porcelain crucible. When cold, the salt is dissolved in hot water, and the gold dried, ignited, and weighed. Copper is the only impurity, and occurs in traces. For its determination, the gold is precipitated from the hydrochloric acid solution of the gold salt by warming with pure ferrous sulphate or ferrous chloride solution, and the copper precipitated in the filtrate by hydrogen sulphide.

APPENDIX

Methods prescribed by the British Pharmacopœia (1914) for the Colorimetric Estimation of Lead and Arsenic in Officinal Salts (and Acids).[1]

I. **Estimation of Lead.**—This test is applied chiefly to salts of sodium, potassium, ammonium, lithium, magnesium, and calcium. It consists in treating a solution of the salt under standardised conditions with sodium sulphide and matching the tint in the manner described below.

Four solutions are required: (1) Strong lead solution: 0·16 g. of lead nitrate and 50 c.c. of strong nitric acid diluted to 100 c.c. One c.c. = 0·001 g. Pb. (2) Dilute lead solution: 1 c.c. of the preceding diluted to 100 c.c. One c.c. = 0·00001 g. Pb. (3) Cyanide solution: a 10 per cent. solution of 10 g. of potassium cyanide treated with 2 c.c. of hydrogen peroxide, which should remain colourless when tested with the dilute lead solution. (Addition of cyanide prevents interference of copper.) (4) Sulphide solution: a 10 per cent. solution of sodium sulphide. Lead-free glass vessels and stock bottles must be used throughout.

Two solutions of the salt to be tested are required: the primary solution (P), containing 12, 7, or 4 g. of the salt, according to solubility and lead content; and the auxiliary solution (A) containing 2 g., both in distilled water. Each solution is filtered (if necessary) into a 50 c.c. Nessler tube and treated with a slight excess of ammonia and 1 c.c. of the cyanide solution. If now P is darker than A, the tints may be equalised by addition of a very dilute solution of burnt sugar to A.

Both solutions are diluted to 50 c.c., and 2 drops of the sulphide solution stirred in. Titration of A with the dilute lead solution will guide the operator in matching the colour of P by adding a suitable volume of the dilute lead solution to a fresh A solution and putting this once more through the whole process; the method is one by trial and

[1] Referred to by permission of the General Medical Council.

error. One c.c. of the dilute lead solution is equivalent to 1, 2, or 5 parts of lead per million, according to the quantity of salt (12, 7, or 4 g.) used in the preparation of *A*. Solutions of calcium and magnesium salts are first treated with excess of acetic acid, followed by excess of ammonia and 1 c.c. of cyanide solution; magnesium carbonate is dissolved by boiling with acetic acid.

The method prescribed by the Pharmacopœia does not take into account the disturbing effect of ferric salt, a rather common impurity, which will cause a deepening of the colour.

II. **Estimation of Arsenic.**—Arsenic must be determined in iron, zinc, copper, and bismuth salts, as well as in salts of the lighter metals enumerated under I. The colorimetric method is based upon the conversion of the arsenic by nascent hydrogen into hydrogen arsenide and the action of the latter upon mercuric chloride paper: a yellow stain is produced, the intensity of which is compared with that of a series of standard stains obtained with known amounts of arsenic. It should be noted that the expression "parts of arsenic per million" as used in the Pharmacopœia denotes parts of arsenic trioxide per million.

Those undertaking the examination of chemicals destined for officinal use should consult the Pharmacopœia for the various methods of preparing the solutions of the preparations to be tested for arsenic, the standard reagents required, and the dimensions and manipulation of the apparatus.

For ordinary factory control, the evolution flask and procedure described by Hollins[1] may be used with advantage (*cf. also* Vol. I., pp. 433-448).

[1] *J. Soc. Chem. Ind.*, 1917, 36, 576.

POTASSIUM SALTS

By J. T. DUNN, D.Sc., F.I.C., Consulting Chemist,
Newcastle-on-Tyne

GENERAL METHODS FOR THE DETERMINATION OF POTASSIUM

OF the methods used for the determination of potassium, that of Fresenius, in which the potassium is separated as potassium platinichloride, is the most important, and has found general acceptance in the potassium salt industry. Amongst other methods, the determination of potassium as perchlorate, which has been very thoroughly worked out by Wense[1] and by Caspari,[2] may be regarded as of equal value with the older platinum method, a statement substantiated by the fact that the International Congress for Applied Chemistry (1903) decided to class it as an international method of determination, together with the Fresenius method.

A. The Potassium platinichloride method.—In the separation of potassium as potassium platinichloride by Fresenius' shortened method, which has been thoroughly worked out by Precht,[3] the use of pure platinic chloride solution is of the utmost importance. It must be free from platinous chloride and oxides of nitrogen, and contain at most only a small quantity of free hydrochloric acid. Precautions must also be taken against the introduction of other impurities, such as sulphuric acid from impure reagents, and potassium platinichloride from the incomplete washing of recovered platinum from platinum residues. The preparation of the platinic chloride solution is described below.

For washing potassium platinichloride precipitates absolute alcohol should invariably be used, because, while potassium platinichloride is soluble only to the extent of 1 : 40,000 in absolute alcohol, in 80 per cent. alcohol the solubility increases to 1 : 25,000; and secondly, the double salts of platinic chloride with sodium, calcium, and magnesium met with in course of analysis, are at least as soluble in absolute as in more dilute alcohol—the sodium salt decidedly more so. The more

[1] *Z. angew. Chem.*, 1891, **4**, 691.

[2] *Ibid.*, 1893, **6**, 68; *cf.* also, Kreider, *Z. anorg. Chem.*, 1895, **9**, 342; *Chem. News*, 1895, **72**, 241.

[3] *Z. anal. Chem.*, 1879, **18**, 509.

accurate results claimed as a result of the use of 80 per cent. alcohol are due to a compensation of the greater solubility of the potassium platinichloride in that reagent by impurities in the platinic chloride employed. The proposal to remove the impurities in the potassium platinichloride precipitate by dissolving in hot water and filtering off the impurities, is only partially effective as the precipitate may contain in addition to platinous chloride and insoluble sulphates, barium chloride, arising from the use of an excess in the precipitation of sulphuric acid, and potassium platinichloride introduced by the use of an impure platinic chloride solution: these impurities are naturally not removed from the dissolved precipitate by treatment with hot water. Provided a definite, measured quantity of platinic chloride solution is always added, it is simpler to evaporate about 10 c.c. of the platinic chloride solution to dryness, to take up and wash the residue with alcohol, and to weigh it; the impurities in the reagent are thus determined, and a proportionate weight is then deducted from the weight of potassium platinichloride found.

For the collection of the potassium platinichloride precipitate, either a filter paper or a Gooch crucible is employed. In the Stassfurt works filter paper is invariably used, and preference is given to a Swedish paper[1] which permits of quick filtration and is at the same time sufficiently retentive. Filtration is usually hastened by suction. When frequent daily determinations of potassium have to be carried out, the washing of the precipitates may with advantage be done by means of a 10 litre jar placed about 60 cm. above the bench and fitted with a cork, glass tube and rubber tubing, to which a pinchcock and glass jet are attached, instead of by an ordinary wash-bottle.

For the preparation of platinic chloride, waste alcoholic washings and potassium platinichloride precipitates from previous analyses are generally used. The alcoholic washings are diluted with one-third of their volume of water and, after addition of sodium carbonate, heated to boiling on the water-bath in a large porcelain dish, and the potassium platinichloride to be reduced gradually stirred in. The heating and the addition of sodium carbonate must be continued until the liquid above the reduced platinum is perfectly clear, alkaline, and of a faint yellow colour. The solution is then decanted off and the reduced platinum purified by boiling with hydrochloric acid and then with water, evaporating to dryness on the water-bath, and decomposing any organic platinum compounds present by careful ignition. After ignition, the finely ground platinum is boiled once with concentrated nitric acid, the liquid decanted off, and the platinum dissolved in a large porcelain dish on the water-bath by the gradual addition of about four times its weight of warm hydrochloric and nitric acids, in the proportion

[1] J. H. Munktell, No. 1, F. 9 cm.

of four parts of hydrochloric acid to one part of nitric. When solution is complete, the liquid is evaporated till a drop taken out on a glass rod solidifies. Towards the end of the evaporation, water and hydrochloric acid are added alternately to remove nitrous compounds, and fuming hydrochloric acid with very little nitric acid to convert any platinous into platinic chloride. To ensure complete removal of these compounds, the solution may be shaken with a few c.c. of 10 or 20 per cent. solution of pure hydrogen peroxide before dilution. After cooling, the crystalline mass of platinic chloride is taken up with water, the solution filtered and diluted so that 10 c.c. contains 1 g. of platinum (sp. gr. 1·18).

Platinum residues, either washings or precipitates, may also be reduced by zinc dust.

Should scrap platinum be used for the preparation of the chloride, the possible presence of iridium necessitates the addition of ammonium chloride to precipitate the platinum salt, which is then reduced. The purity of the platinic chloride solution is best checked against a solution of 7·64 g. of pure potassium chloride and 1·2 g. of sodium chloride made up to 500 c.c.

For the analysis 0·2 to 1·0 g. of substance is taken, according to its potassium content, dissolved in 10 to 20 c.c. of water in a porcelain dish of about 10 cm. diameter, platinum chloride solution is added in sufficient excess (for the quantities given, say 6 c.c., the excess facilitates the washing), and the liquid evaporated on the water-bath. During evaporation the contents of the dish are frequently agitated and the evaporation continued to dryness, as anhydrous sodium platinic chloride is more soluble in alcohol than the salt with water of crystallisation. The formation of large crystals of sodium platinichloride should be prevented if possible, since they render thorough washing more difficult. The cold residue is moistened with alcohol, and broken down with a flat-headed glass rod, then thoroughly ground up with about 20 c.c. of alcohol, and the washings filtered through a tared filter paper previously dried for about one hour (till constant) at 120° to 130°, weighed warm, and moistened with alcohol before filtering. Since some kinds of filter paper gain weight (2 to 5 mg.) on moistening with alcohol and subsequent drying, it is advisable to moisten the filter with alcohol, and then dry and weigh it before use. Care must be taken in filtering to prevent the liquid from coming in contact with the edge of the filter paper. Two or three similarly conducted washings with alcohol suffice for the complete removal of the soluble platinum double salts. This end is more quickly attained if, after the second addition of alcohol, the dish is warmed on the water-bath till the alcohol nearly boils. A low result need not be feared from this treatment, since the greater part of the substances which cause the hot alcohol to dissolve the

potassium platinichloride is removed by the first cold decantation. The washed precipitate is then brought on to the filter paper, and after as much alcohol has been pumped off as possible, is pressed between filter paper, dried till constant at 120° to 130°, and weighed warm. Twenty minutes generally suffices for the drying.

Before drying, the filter paper is conveniently folded, as shown in Figs. 48 (front view) and 49 (back view); the possibility of any precipitate falling out is thus prevented.

The following *modifications of the platinum method* have been proposed :—

Vogel and Häfcke,[1] in potassium salts containing sulphates, treat the sulphates of the alkalis with a slight excess of platinic chloride, a method previously suggested by Finkener. For the analysis of kainite, for instance, 10 g. of the salt is dissolved in 300 c.c. of water in a 500 c.c. flask, boiled, and, after cooling, the contents made up to the 500 c.c. mark. Fifty c.c. (1 g.) of the solution is evaporated to

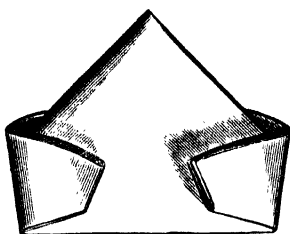
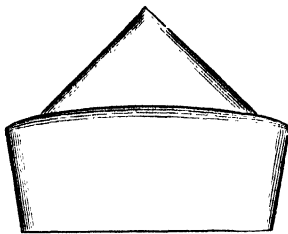



FIG. 48. FIG. 49.

dryness in a platinum dish, and after cooling 20 c.c. of a solution of neutral ammonium carbonate (Schaffgotsch's solution) added to precipitate calcium and magnesium. The bulky precipitate first formed goes into solution on vigorous stirring, a crystalline precipitate separating later. The separation of the calcium and magnesium requires about twelve hours. The liquid is then filtered through a small filter paper and the precipitate washed with 10 to 15 c.c. of Schaffgotsch's solution. The filtrate, after addition of a few drops of sulphuric acid, is evaporated to dryness in a platinum dish, the dish being covered with a clock-glass to prevent spitting of the contents. The residue is then gently ignited to remove ammonium salts, dissolved in hot water, filtered through a small filter paper into a porcelain dish about 10 cm. in diameter, platinic chloride and some hydrochloric acid added, and the whole evaporated to a syrupy consistency. The residual cold, crystalline mass is rubbed up finely with 20 to 25 c.c. of a mixture of 2 parts of absolute alcohol and 1 part of ether, filtered through a

[1] *Landw. Versuchs-Stat.*, xi., vii., 97.

Gooch crucible, and washed until the washings are colourless. The residue remaining in the crucible, consisting of potassium platinichloride and sodium sulphate, after being dried for five to ten minutes in a drying oven, is decomposed in a current of hydrogen, the crucible being fitted up like a Rose crucible, care being taken that the temperature does not rise much above 250°. As a rule, the reduction is complete in from ten to fifteen minutes. The reduced platinum is washed in the same crucible with hot water. The crucible is then dried, ignited, weighed, and the content of potassium calculated.

While from a theoretical standpoint nothing can be said against this method, it is not so favoured by technical chemists as the older, shortened platinum or perchloric acid methods, on account of the more lengthy and complicated manipulation involved. The long time necessary (twelve hours) for the precipitation of the calcium and magnesium renders the method unsuitable, when, as is usual, results are demanded at short notice. It finds its most useful application in the determination of potassium in organic substances. An advantage of the method lies in the small amounts of platinic chloride and of alcohol used.

To avoid weighing the potassium platinichloride it may be decomposed by reducing substances such as formic or oxalic acids, magnesium or zinc dust, and either the separated platinum determined or the chlorine titrated in the filtrate. Thus Fabre[1] reduces the dissolved potassium platinichloride with magnesium powder in warm solution, filters off the platinum and the excess of magnesium powder, and estimates the chlorine in the filtrate volumetrically. Diamant[2] uses zinc dust; the reduction then takes place in the cold. This obviates the formation of insoluble magnesium oxychloride, which is apt to be formed when magnesium is used for the reduction, and which has to be removed by addition of sulphuric acid and the excess of acid subsequently neutralised by calcium carbonate.

Lindo-Gladding's method for the determination of potassium in potassium salts, which is much used in the United States, has not given very satisfactory results in the hands of most chemists.[3] In this method the initial conversion of the sulphates into the corresponding chlorides is avoided by taking a measured portion (0·5 g. in solution) and treating it with 0·25 g. of sodium chloride and a few drops of hydrochloric acid, evaporating with 15 c.c. of platinic chloride solution (1 : 10), washing the residue with alcohol (80 per cent.) till free from sodium platinichloride, and finally with an ammonium chloride solution prepared as follows:—"To a solution of 100 g. of ammonium chloride

[1] *Chem. Zeit.*, 1896, **20**, 502. [2] *Ibid.*, 1898, **22**, 99.

[3] *Cf.* Breyer and Schweitzer, *Z. anal. Chem.*, 1896, **35**, 687; and, Robinson, *J. Amer. Chem. Soc.*, 1894, **16**, 364.

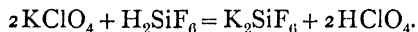
in 500 c.c. of water, 10 g. of potassium platinichloride is added, and after frequent vigorous shaking at intervals during six to eight hours, allowed to stand over night, and filtered." The potassium platinichloride is washed quite free from sulphates with this solution, then again with 80 per cent. alcohol, and finally dried and weighed.

B. The Perchloric acid method.—This method possesses an advantage over the platinichloride method in being more suitable for the analysis of sulphates, and is coming more and more into use. The perchlorates of sodium, calcium, and magnesium, as well as that of barium, are soluble in alcohol, so that a slight excess of barium chloride used for the precipitation of the sulphates is not disadvantageous, as it is completely converted into perchlorate during the analysis. In the platinum method, on the contrary, any excess of barium chloride must be avoided, because, as Precht[1] has shown, barium platinichloride is decomposed by alcohol, and the insoluble barium chloride formed would be weighed with the potassium platinichloride.

Potassium perchlorate being granular, is easily filtered and washed; further, the evaporation after precipitation may be carried further than in the platinum method without disadvantage, and is in fact desirable, so as to convert the chlorides completely into perchlorates. The perchloric acid method is also less costly than the platinum method, and avoids those injurious effects which at times occur in working up platinum residues.

For the preparation of perchloric acid, potassium perchlorate or chlorate is employed. Perchloric acid is prepared according to Caspari[2] as follows:—

Potassium chlorate is heated in a Hessian crucible, 15 cm. high, until the molten mass thickens to a pasty condition showing the end of the decomposition to perchlorate. The ground-up melt is then boiled with one and a half times its weight of water, the potassium chloride solution poured off when cold, the residue washed with cold water to complete the removal of the potassium chloride, and dried. The potassium perchlorate is then converted into perchloric acid by decomposition with hydrofluosilicic acid, according to the equation:—

$$2KClO_4 + H_2SiF_6 = K_2SiF_6 + 2HClO_4.$$

The potassium perchlorate is dissolved in about seven times its weight of hot water in a large porcelain dish, and a slight excess of hydrofluosilicic acid stirred in. The boiling is continued until all small, hard lumps of potassium perchlorate have disappeared, the evaporated water being made up by fresh additions. After cooling, the solution is filtered or decanted from the gelatinous potassium fluosilicate and concentrated as far as possible on the water-bath; after standing in a cold

[1] *Z. anal. Chem.*, 1879, **18**, 516. [2] *Loc. cit.*

place for twenty-four hours, any potassium fluosilicate remaining in solution, along with a small quantity of potassium perchlorate, separates out. The solution is then filtered through an asbestos filter, diluted with an equal volume of water, and any remaining hydrofluosilicic acid and sulphuric acid, which may be present as an impurity from the hydrofluosilicic acid, precipitated with barium chloride. When the solution has cleared, it is filtered and evaporated till all hydrochloric acid fumes are driven off and white fumes of perchloric acid appear. On cooling, a further portion of potassium perchlorate and needles of sodium perchlorate separate out, from which the free concentrated acid is filtered off. The filtrate is finally diluted with an equal volume of water and allowed to stand for from one to two days, during which time any remaining barium fluosilicate and barium sulphate separate out. After further filtration the reagent is ready for use.

Kreider[1] gives the following method for the preparation of perchloric acid :—

One hundred to three hundred g. of sodium chlorate is heated in a glass retort until the evolution of oxygen begins. After about one to two hours the molten mass becomes solid, showing that the decomposition of chlorate into perchlorate and chloride is complete. After cooling, the mass is washed out into a large porcelain dish, and treated with sufficient hydrochloric acid to decompose any remaining chlorate. The whole contents of the dish are then evaporated to dryness, either on the water-bath or over a free flame, being continually stirred during the evaporation. The broken-up residue is then treated with an excess of the strongest hydrochloric acid; perchloric acid and sodium chloride are formed, which are separated by filtration through a Gooch crucible. The filtrate is evaporated on the water-bath until all the hydrochloric acid is removed and white fumes of perchloric acid begin to come off.

It is not now necessary to prepare the acid in the laboratory, as it may be purchased in 20 per cent. solution; but it must be ascertained that it leaves no residue on evaporation to dryness, and should it do so it must be redistilled. It should give no reaction with barium chloride (fluosilicates), and 10 c.c. should mix without turbidity with 10 c.c. of 96 per cent. alcohol.

According to van Enester,[2] the strength of perchloric acid solutions varies with the specific gravity as follows :—

Per cent. of $HClO_4$	Sp. gr. 15°/4°	Per cent. of $HClO_4$	Sp. gr. 15°/4°
20	1·125	50	1·410
30	1·210	60	1·540
40	1·300	70	1·675

[1] *Amer. J. Sci.*, 1895, **49**, 443; *Chem. News*, 1896, **73**, 8, 17.
[2] *Z. anorg. Chem.*, 1907, **52**, 270.

D. V. Hill[1] has suggested the use of aniline perchlorate instead of perchloric acid.

To carry out the determination, substance equivalent to 0·4 or 0·5 g. of potassium chloride is dissolved in about 20 c.c. of water, and evaporated on the water-bath in a flat, dark-blue glazed porcelain dish 10 cm. in diameter, with 5 c.c. of perchloric acid of 1·125 sp. gr. (20 per cent. of $HClO_4$), till the smell of hydrochloric acid ceases and white fumes of perchloric acid are evolved. The residue when cold is carefully triturated with 20 c.c. of 96 per cent. alcohol containing about 0·2 per cent. of perchloric acid solution. After allowing to settle for a short time, the supernatant liquid is filtered through a paper prepared as in the platinum method, or through a Gooch crucible. The trituration is repeated twice, and the residue then removed on to the paper or crucible, and subsequently washed with the mixture of perchloric acid and alcohol. The perchloric acid is finally removed from the filter and precipitate by washing with the smallest possible quantity of pure 96 per cent. alcohol. The precipitate is then dried and weighed as in the platinum method.

Devices for lessening the solubility of potassium perchlorate in the washing liquid have received a good deal of attention. Davis[2] recommends washing with alcohol saturated with the salt, and his proposal is approved by Thin and Cumming,[3] who also point out that the solubility decreases considerably as the percentage of alcohol rises above 95, and by Baxter and Kobayashi,[4] who use absolute alcohol, and wash the precipitate at or near 0°. Gooch and Blake,[5] on the other hand, consider that a saturated solution of potassium perchlorate containing also sodium perchlorate, may, in contact with solid potassium perchlorate, deposit some of its potassium salt, and they therefore prefer to use 97 per cent. alcohol containing 0·1 per cent. of perchloric acid, taking care to keep down the bulk of washing liquid as far as possible. Baxter and Kobayashi[6] confirm this, and suggest that the sodium salt should be removed by washing with alcohol containing perchloric acid, before the washing with alcohol saturated with potassium perchlorate is begun.

Caspari suggested dissolving the precipitate after the first washing, and evaporating afresh with perchloric acid, to effect complete removal of sodium salt; his proposal is supported by Baxter and Kobayashi, and also by Gooch and Blake, who consider the operation imperative when the precipitate weighs more than 0·3 g.

[1] *Amer. J. Sci.*, 1915, **40**, 75; *Analyst*, 1916, **41**, 55.
[2] *J. Agric. Sci.*, 1912, **5**, 52; *Analyst*, 1913, **38**, 47.
[3] *J. Chem. Soc.*, 1915, **107**, 361.
[4] *J. Amer. Chem. Soc.*, 1917, **39**, 249.
[5] *Amer. J. Sci.*, 1917, **44**, 381; *Analyst*, 1918, **43**, 277.
[6] *J. Amer. Chem. Soc.*, 1920, **42**, 735; *Analyst*, 1920, **45**, 238.

R. L. Morris,[1] in a comprehensive paper, recommends the following procedure:—The solution of the potassium salt is evaporated with perchloric acid, three times in all, and in the third evaporation is taken to dryness. The residue is treated with 10 c.c. of wash liquid (98 per cent. alcohol, 100 c.c.; 20 per cent. perchloric acid, 1 c.c.), stirred well with a flat-headed glass rod, allowed to stand 10 to 15 minutes if sodium is present, occasionally stirring; allowed to settle, and the liquid decanted through asbestos in a Gooch crucible. If sodium is absent, the precipitate is now rinsed into the filter, using a measured quantity of liquid in a wash-bottle. If sodium is present, the basin and precipitate are placed on top of the air-oven till all alcohol is removed, the precipitate is dissolved in the least possible amount of boiling water, and the liquid again evaporated to dryness. Treatment with 10 c.c. of wash liquid and decantation are repeated, and the precipitate is washed into the filter with the help of the last 10 c.c. of filtrate, and washed on the filter by a measured volume of wash liquid added in small portions. Crucible and contents are now dried at 130° to 150°, cooled, and weighed. Then 2 or 3 c.c. of wash liquid are passed through, and the drying and weighing repeated. This is done till two successive weighings do not differ by more than 2 or 3 tenths of a milligram.

The solubility of potassium perchlorate in absolute alcohol containing varying amounts of perchloric acid was determined by Baxter and Kobayashi to be as follows:—

Per cent. of $HClO_4$ (used in 60 per cent. solution).	Grammes of $KClO_4$ dissolved per 100 c.c., at 0°.	21°.
0	0·0047	0·0080
0·05	0·0019	0·0040
0·10	0·0019	0·0030
0·15	0·0018	0·0028
0·20	0·0018	0·0026
0·30	0·0019	0·0031

whilst Thin and Cumming, working at 25° with alcohol of different strengths, obtained the following figures:—

Per cent. of $HClO_4$ (used in 20 per cent. solution).	Strength of alcohol.	Grammes of $KClO_4$ dissolved per 100 c.c.
0·0	93·5	0·051
0·2	93·5	0·018
0·0	98·8	0·019
0·2	98·8	0·010
2·0	98·8	0·028

[1] *Analyst*, 1920, 45, 349.

C. Other Methods for the determination of Potassium.—The separation of potassium as *potassium hydrogen tartrate* has been much improved by Frank,[1] Fleischer,[2] and especially by Bayer.[3] To the solution of about 0·7 g. of the substance containing potassium in 25 c.c. of water, Bayer adds sodium carbonate equivalent to the amount of acid radicle present, and then excess of acetic acid (6 c.c. of 80 per cent. acid) and tartaric acid (about 2·4 g. of the solid). Absolute alcohol is then added to the heated solution until it contains 25 per cent. of alcohol. After standing for two hours, the cleared solution is filtered off, the precipitate freed from sodium bitartrate by washing with 25 per cent. alcohol, and finally washed with 50 per cent. alcohol. The precipitate along with the filter paper is then titrated with $N/10$ sodium hydroxide, using phenolphthalein as indicator. A correction is added for the solubility of the potassium salt in the washing liquors (none for the original liquid) of 1·2 c.c. of $N/10$ alkali per 100 c.c. of 50 per cent., 3·5 c.c. per 100 c.c. of 25 per cent. alcohol.

Rose[4] proposed the separation of potassium as *potassium silico-fluoride*, by treating the concentrated solution of the potassium salt with an excess of pure hydrofluosilicic acid and an equal volume of alcohol. The gelatinous precipitate of potassium fluosilicate is collected on a weighed filter paper, washed with 50 per cent. alcohol, dried at 100°, and weighed.

Gilbert[5] precipitated the potassium as potassium sodium cobalti-nitrite, with excess of cobaltous acetate and sodium nitrite, washing the precipitate first with a cobalt solution (10 g. crystallised cobaltous acetate and 90 g. pure potassium-free sodium nitrite dissolved in water, 25 c.c. acetic acid (sp. gr. 1·04) added, and the solution made up to 1 litre), and finally with 80 per cent. alcohol. The washed precipitate is then either dissolved by warming with hydrochloric acid, or decomposed at 300° and the residue taken up with water. The solution thus obtained is then further treated, as usual, with platinic chloride or with perchloric acid. However accurate this method may be, the lengthy manipulation involved renders it unsuited to technical purposes.

Gilbert's method is the precursor of methods for the direct determination of potassium by precipitation as potassium sodium cobaltinitrite. This was first recommended by Adie and Wood.[6] They make use of a reagent obtained by dissolving 113 g. of cobalt acetate in 300 c.c. of water and 100 c.c. of acetic acid, and also dissolving 220 g. of sodium nitrite in 400 c.c. of water; these solutions,

[1] *Dingl. polyt. J.*, 1867, **183**, 40.
[2] *Z. anal. Chem.*, 1870, **9**, 331.
[3] *Chem. Zeit.*, 1893, **17**, 686.
[4] *J. prakt. Chem.*, 1867, **102**, 7.
[5] Inaugural dissertation, Tübingen, 1898: *Die Bestimmung des Kaliums nach quantitativer Abscheidung desselben als Kaliumnatriumkobaltnitrit.*
[6] *J. Chem. Soc.*, 1900, **77**, 1076.

after filtration, are mixed, and the nitric oxide produced is removed under a filter-pump. The liquid is then allowed to stand for twenty-four hours, filtered from any precipitate that may have formed, and made up to a litre. The potassium solution should contain between 0·5 and 1·0 per cent. of K_2O; at greater dilutions the precipitate passes through the filter; 10 c.c. of this is precipitated by the addition of 1 c.c. of acetic acid and 10 c.c. of the reagent. After standing overnight the liquid is filtered through a weighed paper or through asbestos in a weighed Gooch crucible, the precipitate washed with 10 per cent. acetic acid, and dried at 125° to constant weight. The dried precipitate has the formula $K_2NaCo(NO_2)_6$.

Instead of weighing the precipitate, the nitrite may be determined volumetrically by permanganate. The precipitate and asbestos are placed in a beaker and boiled with dilute sodium hydroxide solution; the liquid is filtered from the asbestos and cobaltic hydroxide, and the filtrate and washings are made up to 100 c.c. Of this, 20 c.c. is acidified and rapidly titrated with $N/10$ permanganate. A small loss of nitrogen oxides occurs on acidifying; therefore to a second 20 c.c. of the solution is added the amount of permanganate used in the first titration, the liquid then made acid with dilute sulphuric acid, and the titration finished.

W. A. Drushel[1] found that the difficulties of filtration can be overcome, and hence the need for working with potassium solutions between limits of concentration abrogated, by evaporating after precipitation; and also that titration with permanganate can be carried out without previous removal of the cobalt. To the solution, containing not more than 0·2 g. of K_2O, and free from ammonium salts, he adds a large excess of the reagent, and evaporates on the water-bath to pastiness. The mass is then treated with 50-100 c.c. of cold water, stirred till the excess of sodium cobaltinitrite has dissolved, the precipitate allowed to settle, the liquid decanted through a Gooch filter, the precipitate washed two or three times by decantation, and finally on the filter, with cold water. A measured volume (in excess) of $N/10$ permanganate is diluted to about ten times its bulk with water, and heated nearly to boiling. The precipitate and filter are introduced and well stirred, then the crucible is put in. When the solution darkens through precipitation of manganese dioxide, 5 to 25 c.c. of 1 : 7 sulphuric acid is added, stirred in, and the liquid allowed to stand for a few minutes. Then a measured volume (in excess) of $N/10$ oxalic acid, containing 50 c.c. of sulphuric acid per litre, is added, the liquid is kept just below boiling point till clear, and the excess of oxalic acid titrated by permanganate. The oxalic acid should be standardised against permanganate which has been treated as in the analysis. In

[1] *Amer. J. Sci.*, 1907, **24**, 433; *Analyst*, 1908, **33**, 35.

this titration, the oxidation of one twelfth of the nitrite is effected by the reduction of the cobaltic to cobaltous oxide; hence each cubic centimetre of $N/10$ permanganate is equivalent not to 0·000785 g. K_2O, but to twelve elevenths of that amount, or 0·000856 g. Drushel found that salts of calcium or magnesium, or soluble phosphates, do not interfere with the accuracy of the determination.

Modifications in detail of this method have been suggested by L. T. Bowser,[1] O. M. Shedd;[2] F. H. Macdougall,[3] Garola and Braun,[4] and by A. H. Bennett,[5] who uses it to separate potassium from other substances, and then determines the potassium as perchlorate. According to P. Wenger and C. Hémen,[6] the proportion of potassium in the mixed precipitate of sodium and potassium cobaltinitrites can be calculated from the content of cobalt.

Morris[7] found that to obtain accurate and consistent results from Drushel's method it was desirable to heat at least ten minutes before and at least ten minutes after acidifying the permanganate, and to add a good excess of oxalic acid.

The following methods have also been suggested:—The precipitation of the potassium as *potassium picrate*, proposed by Hager,[8] as *potassium bismuth thiosulphate* by Carnot[9] and Campari,[10] and Gay-Lussac's method of determining potassium chloride by the reduction in temperature produced on dissolving potassium chloride and sodium chloride in water.

SPECIAL METHODS OF ANALYSIS

I.—STASSFURT SALTS

A. Crude Salts

These include *Carnallite* (mixture of carnallite, rock salt, and kieserite), *Rock kieserite* (mixture of carnallite and kieserite), *Kainite* (mixture of kainite and rock salt), *Sylvinite* (mixture of sylvite and rock salt), and "*Hartsalz*" (mixture of sylvite, rock salt, and kieserite).

For the examination of the crude salts it is well to take as large a sample as possible.

Determination of Potassium. 1. *Platinum method.* In the Stassfurt laboratories, quantities of the salts to be examined are weighed out, as

[1] *Ind. Eng. Chem.*, 1909, **1**, 791; *J. Chem. Soc.*, 1910, **98**, 999.
[2] *Ibid.*, 1910, **2**, 379; *Analyst*, 1910, **35**, 499.
[3] *J. Amer. Chem. Soc.*, 1912, **34**, 1684; *Analyst*, 1913, **38**, 81.
[4] *Ann. Falsif.*, 1917, **10**, 572; *Analyst*, 1918, **43**, 150.
[5] *Analyst*, 1916, **41**, 165.
[6] *Ann. Chim. anal.*, 1920 [II], **2**, 198.
[7] *Analyst*, 1923, **48**, 250.
[8] *Pharm. Centr.*, **22**, 225.
[9] *Comptes rend.*, 1878, **86**, 478.
[10] *Z. anal. Chem.*, 1884, **23**, 60.

proposed by Precht, so that the calculation of the content of potassium chloride or sulphate from the weight of potassium platinichloride is avoided. One mg. of potassium platinichloride is made to correspond to 0·1 per cent. of potassium chloride or sulphate. Taking the factors[1] for the calculation of the content of potassium chloride, potassium sulphate, or potassium oxide from the potassium platinichloride found as 0·3056, 0·3571, and 0·1931 respectively, suitable multiples of these figures are taken in the original weighings according to whether the percentage of potassium chloride or sulphate is required. This plan has the further advantage that the quantity of platinic chloride to be added is independent of whether the content is calculated to potassium chloride or to potassium sulphate.

The potassium in crude potassium salts is determined as follows:— 30·56 g. of carnallite or of rock kieserite, or 35·71 g. of kainite, sylvite, or hartsalz, is dissolved in a 500 c.c. flask by boiling with 300 c.c. of water with addition of 15 c.c. of concentrated hydrochloric acid, and after cooling, diluted up to the mark. Usually, and if the sample is finely ground, 7·640 g. and 8·9275 g. respectively suffice for the analysis. The crude salts may be dissolved in pure water or in water containing hydrochloric acid, but as hydrochloric acid must be added before precipitating the sulphuric acid, it can be added to the water at this stage. Fifty c.c. of the solution, previously filtered if necessary, is treated in a 200 c.c. flask with barium chloride, as described on p. 417, filled up to the mark after cooling, and 20 c.c. of the filtrate (=0·3056 or 0·3571 g. of substance) used for the potassium determination, which is carried out as described on p. 401.

2. *Perchloric acid method.* 13·4525 g. of carnallite or rock kieserite, or 15·7218 g. of kainite, sylvite, or hartsalz, is dissolved by heating to boiling with 300 c.c. of water and 15 c.c. of concentrated hydrochloric acid in a 500 c.c. flask, and normal barium chloride solution (122 g. of $BaCl_2, 2H_2O$, and 50 c.c. of concentrated hydrochloric acid in 1000 c.c.) added in slight excess. The quantities required are, for carnallite, about 20 to 40 c.c., and for kainite, 65 to 80 c.c. After cooling, the contents of the flask are made up to the mark and filtered through a double, dry, pleated filter paper about 18 cm. in diameter. Twenty c.c. of the filtrate (0·5382 or 0·6289 g. of substance) is treated with perchloric acid as described on p. 406.

One mg. of potassium perchlorate corresponds in this way to 0·1 per cent. of potassium chloride or sulphate.

[1] These factors are based on the results of prolonged experience at Stassfurt, and are in accord with the most accurate data obtained independently by other investigators. The precipitate obtained is not pure K_2PtCl_6, as it retains some combined water, which is not given up, even on prolonged heating; on this account the factors are somewhat lower than would correspond to the actual atomic weight, 195·23 for platinum. See also Roemer, *Chem. News*, 1910, **101**, 54.

Determination of Magnesium chloride.[1] The magnesium chloride of carnallite is easily extracted by alcohol, whilst that of kainite is not dissolved. A simple method for distinguishing between "non-carnallitic" crude salts and "carnallitic" salts is based on this difference.

Ten g. of the finely ground crude salt is vigorously shaken for ten minutes in a 250 c.c. flask with 100 c.c. of 96 per cent. alcohol, and 10 or 20 c.c. of the alcoholic filtrate titrated with $N/10$ silver nitrate solution. Those salts which contain more than 6 per cent. of chloride soluble in alcohol are classed as "carnallitic," and those containing 6 and less per cent. as "non-carnallitic."

Determination of the Total Magnesium. The following is a very accurate method, introduced by Precht,[2] for the determination of magnesium salts, and is applicable to kieserite: 10 g. of the finely ground crude salt is boiled for not less than one hour in a 500 c.c. flask about two-thirds filled with water; after cooling, a measured volume (50-60 c.c.) of $2N$ potassium hydroxide is added, and, if much calcium is present, 20 c.c. of a neutral solution of potassium oxalate (1 : 10). The flask is then filled up to the mark, and the solution filtered after standing a quarter of an hour. Fifty c.c. of the filtrate is then titrated back with $N/10$ sulphuric acid. An empirical correction of 1·2 per cent. must be added to the content of magnesium sulphate found.

Volumetric determination of the Sulphuric acid. The method worked out by Wolf Müller,[3] first alone, and later in collaboration with K. Dürkes,[4] for the titration of sulphuric acid by means of benzidine hydrochloride, may be used with advantage in the examination of potassium salts. The determinations are trustworthy, and are quickly and easily carried out (*cf.* Vol. I., p. 374).

Complete Analysis of the Crude Salts

One hundred g. of the sample is dissolved in about 500 c.c. of water, the solution filtered, and the filtrate and washings diluted to 1 litre. One portion of the solution is set aside for the determination of the sulphuric acid, and another portion for that of the calcium and magnesium. For the determination of the chlorides of the alkalis, 100 c.c. of the solution (= 10 g. of substance) is acidified with hydrochloric acid, heated to boiling, and the sulphates completely precipitated in a 500 c.c. flask with barium chloride, avoiding an excess of the precipitant. The solution is diluted to the mark and 50 c.c. (= 1 g. of substance) evaporated to dryness to drive off the hydrochloric acid, and the magnesium chloride then decomposed by igniting

[1] *Z. anal. Chem.*, 1879, **18**, 438.
[2] *Ibid.*
[3] *Ber.*, 1902, **35**, 1587.
[4] *Z. anal. Chem.*, 1903, **42**, 477.

with oxalic acid. After ignition, the residue is moistened with a small quantity of ammonium carbonate to convert the calcium oxide formed into carbonate. The chlorides of the alkalis are dissolved out by water from the calcium and magnesium carbonates, the solution is filtered, and the filtrate evaporated and the residue weighed. The potassium chloride in the mixed chlorides is then determined either by platinic chloride or by perchloric acid in the usual way. The weight of mixed chlorides, less the amount of potassium chloride, gives the content of sodium chloride. The constituents of the crude salts insoluble in water are determined by treating 10 g. of the salt with hot water, and filtering off the insoluble matter on to a tared filter paper, which is then dried at 100° and weighed. For the determination of water, 10 g. is weighed into a platinum crucible, covered with a weighed quantity of ignited lead oxide, and heated with the lid on for ten minutes over a small flame to a dull red heat; the loss after ignition gives the water content. Or 10 g. is ignited, the loss determined, the ignited mass dissolved in water, and the dissolved chlorine determined volumetrically, in order to find how much magnesium chloride was decomposed by the ignition. The difference between the chlorine content before and after ignition, allowing for the gain in oxygen, is deducted from the loss on ignition; the remainder of the loss is water.

In kainite, the proportion of the salts is calculated by subtracting, from the total quantity of soluble sulphuric acid, the amount of sulphuric acid corresponding to the calcium found. The remaining sulphuric acid is divided into two equal parts, and calculated to potassium sulphate and magnesium sulphate in the molecular proportions in which these salts are present in kainite and in picromerite respectively. The magnesium not combined as sulphate is calculated as chloride, and any remaining potassium is taken as potassium chloride. These calculations indicate on the one hand how much potassium is present as kainite ($K_2SO_4 . MgSO_4 . MgCl_2 . 6H_2O$), and as picromerite ($K_2SO_4 . MgSO_4 . 6H_2O$), and on the other hand how much is present as potassium chloride. Any sodium present is reckoned as sodium chloride. In hartsalz, in which the water content (up to 5 per cent.) amounts to only about one-third of that in kainite, the potassium is reckoned as chloride. If langbeinite ($K_2SO_4 . 2MgSO_4$) is present as an impurity, the magnesium and any calcium are calculated as sulphates, and any excess of sulphuric acid as potassium sulphate. In dealing with the examination and recognition of complicated mixtures of salts, the determination of the individual constituents does not suffice. The amount of magnesium chloride soluble in alcohol must then be determined, and the content of carnallite deduced therefrom, and a separation of the constituents by means of specific gravity must also be made. If the individual constituents in the salts of different specific gravity are then determined,

the composition of the original mixture can be calculated from that of the different salts. The separation by means of specific gravity is carried out by mixing the finely ground mixture of salts with a solution of benzene and bromoform, so proportioned that the whole of the salts sink to the bottom of the vessel; by gradually increasing the specific gravity of the liquid by the addition of bromoform, the lighter particles rise successively to the top and can be collected.

B. Intermediate Products of Manufacture

The examination of the intermediate products, liquors, residues, etc., arising in the working up of the crude salts into concentrated potassium salts, is carried out by the methods described above for the crude salts. Should these products contain but little potassium and much sodium chloride, Finkener's method of separation may be used with advantage. The solution containing the potassium salts is treated, without previous separation of sulphates, with only just sufficient platinic chloride to precipitate the potassium; after washing the evaporated residue, the potassium platinichloride is reduced and weighed as platinum.

C. Manufactured Products

1. Potassium Chloride.

Determination of Potassium. 1. *Platinum method.* 7·640 g. of the finely ground sample is dissolved and made up to 500 c.c. In salts containing more than 0·5 per cent. of sulphuric acid (SO_3), the previous conversion of the sulphates into the corresponding chlorides by means of barium chloride containing hydrochloric acid is necessary. Twenty c.c. (=0·3056 g. of the salt) of the solution or filtrate is then evaporated with 5 c.c. of platinic chloride solution. The evaporation may be continued to dryness without risk; this treatment differs from that of the crude salts, since, together with the potassium platinichloride, which constitutes the bulk of the residue, only sodium platinichloride is present, which is more readily dissolved by alcohol when dehydrated.

The further treatment of the residue is carried out as described for the crude salts. The use of hot alcohol for washing is also strongly advocated in this instance. One mg. of potassium platinichloride corresponds to 0·1 per cent. of potassium chloride.

2. *Perchloric acid method.* 13·455 g. of the finely ground sample is dissolved in water, 3 to 4 c.c. of barium chloride solution containing hydrochloric acid (p. 417) added, and the whole then made up to 500 c.c. To 20 c.c. (=0·5382 g. of the salt) of the filtrate is added

one and a half times the quantity of perchloric acid necessary for the decomposition of all the salts, the solution evaporated on the water-bath, and the residues treated as described under "Crude Salts." One mg. of potassium perchlorate corresponds to 0·1 per cent. of potassium chloride.

Determination of the Sodium chloride in high percentage Potassium chloride. The following method for the determination of the sodium chloride should only be used in dealing with 95 to 99 per cent. potassium chloride. It is a modification of the method recommended by Röttger and Precht,[1] and depends on the solubility of sodium chloride in alcohol being greater than that of potassium chloride. The solubilities are as follows:—

At 15°, 100 parts of alcohol of:—

	90 per cent.	92.5 per cent.	95 per cent. by weight
dissolve	0·345	0·223	0·146 parts of sodium chloride
and	0·073	0·043	0·028 parts of potassium chloride.

According to the Röttger-Precht method, 20 g. of the finely ground potassium chloride is vigorously shaken for half an hour in a 100 c.c. flask with about 80 c.c. of 90 per cent. alcohol (or a sufficient quantity to dissolve the whole of the sodium chloride present). Any magnesium salts present are precipitated by the addition of 0·5 c.c. of a 10 per cent. potassium carbonate solution, the whole again vigorously shaken and made up to the mark with 90 per cent. alcohol. Fifty c.c. (= 10 g. of the salt) is evaporated to dryness in a platinum dish, gently ignited, and weighed; the potassium chloride is determined in the residue, and the sodium chloride present in the original salt estimated by difference.

In order to obviate the prolonged shaking of the salt with 90 per cent. alcohol and to bring about rapid solution of the sodium chloride, the following procedure is adopted in the laboratories of the German Potash Syndicate:—

12·5 g. of potassium chloride is dissolved in a 250 c.c. flask by boiling with 25 c.c. of water in which about 90 mg. of potassium carbonate is dissolved. A larger excess of potassium carbonate may bring about a partial re-separation of the dissolved sodium chloride. Absolute alcohol is added to the hot solution, the whole well mixed, made up to the mark, and shaken vigorously for about one minute. One hundred c.c. (= 5 g. of salt) of the filtered solution is evaporated to dryness in a platinum or porcelain dish, after addition of a few drops of concentrated hydrochloric acid to neutralise the dissolved potassium carbonate. The residue is then gently ignited and weighed. In the mixture of potassium and sodium chlorides thus obtained, the potassium chloride is either

[1] *Ber.*, 1885, **18**, 2076; *J. Soc. Chem. Ind.*, 1886, **5**, 40.

determined by means of platinic chloride or perchloric acid and the sodium chloride taken by difference, or the total chlorine content is determined volumetrically by titration with *N*/10 silver nitrate solution, and the amounts of potassium chloride and sodium chloride calculated.

Determination of Magnesium chloride or of Magnesium salts in Potassium chloride. For this purpose 25 g. of the salt is dissolved in a 500 c.c. flask and 10 c.c. of 2*N* potassium hydroxide added. After filling up to the mark, shaking and filtering, 50 c.c. of the filtrate is titrated with *N*/10 sulphuric acid. Any calcium compounds remaining in solution do not influence the result.

The precipitation of the magnesium salts by means of calcium saccharate, whereby magnesium oxide and not magnesium saccharate is formed, may also be used for the determination. This method is adopted at the Salzbergwerk Neustassfurt. The procedure is as follows :—

Twenty-five g. of the salt is treated with 150 to 200 c.c. of water in a 250 c.c. flask, 25 c.c. of a calcium saccharate solution of known strength added, the whole well shaken and diluted to 250 c.c. The bulky precipitate of magnesia is filtered off after a short time through a pleated filter paper, and 50 c.c. of the filtrate titrated with *N*/10 sulphuric acid, using phenolphthalein as indicator.

The calcium saccharate solution is best prepared by adding 450 g. of calcium oxide and 450 g. of sugar to 7 litres of water; after shaking vigorously for half an hour the liquid is allowed to stand for two to three weeks, then filtered, and a further 450 g. of sugar added. Access of air should be avoided both in the use and in the storage of the solution.

Determination of Water. This determination is carried out in the same manner as that described for the crude salts, except that the covering layer of lead oxide is only employed with salts rich in magnesium chloride.

Determination of Insoluble Matter. To estimate the ingredients insoluble in water, 10 g. of potassium chloride is dissolved in hot water, and the residue collected on a tared filter paper.

The determinations of *Calcium* and of *Sulphuric acid* are carried out by the ordinary methods.

2. Potassium Sulphate.

General considerations on the analysis of Potassium salts containing a high percentage of Sulphates. In the determination of potassium in compounds containing a high percentage of sulphates, when the potassium is to be separated as platinichloride or perchlorate, the most difficult part of the analysis lies in the precipitation of the sulphuric acid by means of barium chloride. In the platinum method,

a small amount (about 0·5 per cent. of SO_3) of unprecipitated sulphate does not matter, since, as stated above, an excess of barium chloride is to be avoided at all costs on account of the decomposition of barium platinichloride by alcohol. On the other hand, a small excess of barium chloride does not influence the result when the perchloric acid method is employed. If the instructions given below are carefully carried out, an easy and complete separation of the sulphuric acid is effected and accurate results are obtained. In order to prevent the possibility of the barium sulphate carrying down any potassium, the precipitation is effected in strong hydrochloric acid solution (122 g. $BaCl_2, 2H_2O$, with 50 c.c. concentrated hydrochloric acid, diluted to 1000 c.c.); the barium chloride must be free from potassium salts as impurities. In the laboratory of the "Konsolidierte Alkaliwerke zu Westeregeln," the conversion of the sulphates in the crude salts into the corresponding chlorides is carried out in neutral solution as follows: 10 g. of carnallite with about 150 c.c. of water is heated to boiling in a 250 c.c. flask and precipitated with a neutral solution of 127 g. $BaCl_2, 2H_2O$ in 1 litre (1 c.c. = 50 mg. SO_4), which is run in from a burette. The advantage of using this neutral solution is, that complete precipitation of the sulphuric acid is shown by the appearance of the steam bubbles, which remain transparent until the precipitation is complete and then suddenly become opaque. As a precaution, a few more drops of barium chloride solution are then added. After cooling, the flask is filled up to the mark. The errors arising from ignoring the volume of the barium sulphate and from the precipitation being effected in neutral solution compensate one another.

Morris,[1] who bases his procedure on the work of Allen and Johnston (Vol. I., p. 371), gives the following directions for the removal of sulphate in such a way as to avoid loss of potassium: The solution should be neutral, and either contain 1 to 1.5 per cent. of total potassium and sodium salts, or, if much sulphate is present, be diluted so that not much over 2 g. of barium sulphate is obtained per 100 c.c. of the solution. The volume of the solution should be from 40 to 80 c.c.; hydrochloric acid, in amount equal to a ninth of the volume of the solution, is added, the liquid heated to boiling, and the sulphate precipitated by pouring in barium chloride solution in slight excess. After settling, the precipitate is filtered off and well washed, ignited wet, boiled for ten minutes with 50 c.c. of water containing a few drops of hydrochloric acid, filtered off and washed once: the filtrate is added to the main filtrate for the determination of potassium as perchlorate.

Determination of Potassium. 1. *Platinum method.* 8·9275 g. of the finely ground sample is dissolved by boiling in 350 c.c. of water and 20 c.c. of concentrated hydrochloric acid, in a 500 c.c. flask. Barium

[1] *Analyst*, 1923, 48, 250.

chloride is then run into the boiling solution, drop by drop, from a stoppered burette. From the composition of the potassium salt under analysis the amount of barium chloride required for the precipitation of the sulphuric acid is approximately calculated beforehand, so that the greater part of the barium chloride can be added without testing. The final additions are made carefully, and the solution tested from time to time to see how far the precipitation has proceeded. The complete precipitation of the sulphuric acid is most sharply recognised by adding a crystal of barium chloride to the clear, settled solution and noting whether any milkiness is produced. Should a trace of sulphuric acid still be present, the crystal produces a distinct cloudiness which spreads gradually throughout the solution from top to bottom. Any slight excess of barium chloride is removed by the addition of a few drops of sulphuric acid. When the precipitation is complete and the solution cold, the flask is filled up to the mark and 20 c.c. (= 0·3571 g. of the salt) of the filtered solution treated as usual with 5 c.c. of platinic chloride solution (1 ; 10). One mg. of potassium platinic chloride corresponds to 0·1 per cent. of potassium sulphate. To the amount of potassium sulphate found, 0·3 per cent. must be added in the case of potassium sulphate (90 to 97 per cent.); no correction is necessary with potassium magnesium sulphate.

2. *Perchloric acid method.* 15·7225 g. of the salt is dissolved by boiling in 700 c.c. of water and 30 c.c. of concentrated hydrochloric acid in a litre flask ; a 500 c.c. flask is not sufficiently large, on account of the bulk of the barium sulphate precipitate. The further manipulation is the same as given above, with the exception that a small excess of barium chloride may be employed, and 40 c.c. of the filtrate (=0·6289 g. of the salt) is evaporated with the necessary quantity of perchloric acid. One mg. of potassium perchlorate corresponds to 0·1 per cent. of potassium sulphate. To the content of potassium sulphate found, 0·3 per cent. must be added, as above.

The less important constituents of the potassium sulphate or potassium magnesium sulphate (magnesium, calcium, sodium, sulphuric acid, chlorine, water, and insoluble matter) are determined by the usual methods.

3. Potassium Salt Manures.

The analysis of potassium salt manures does not differ essentially from that of potassium sulphate. According to whether the potassium content is to be expressed as potassium chloride or as sulphate, 15·280 g. (if as chloride) or 17·855 g. (if as sulphate) of the salt is taken if the potassium is estimated as platinichloride. Should the perchloric acid method be preferred, the quantities taken are correspondingly altered. The potassium salt manures frequently contain a large amount of matter insoluble in hydrochloric acid, which

renders the end-point in the precipitation of the sulphuric acid difficult to recognise; it is then advisable to filter the hydrochloric acid solution before precipitating. The procedure, using the platinum method, is then as follows:—

15·280 g. or 17·855 g. of the sample is dissolved in water with addition of 10 c.c. of concentrated hydrochloric acid in a 500 c.c. flask, diluted to the 500 c.c. mark, shaken, filtered, and 250 c.c. (= 7·640 g. or 8·9275 g. of the salt) of the filtrate precipitated with barium chloride, as usual, in a 500 c.c. flask, made up to 500 c.c., shaken, filtered, and 20 c.c. of the filtrate evaporated with 6 c.c. of platinic chloride solution (1 : 10). No addition to the content of potassium chloride or sulphate found is necessary.

The determination of the remaining constituents is carried out by any of the above methods. In the determination of moisture a possible high content of magnesium chloride must be borne in mind.

II.—NITRE

A. Raw Materials

1. Chili Saltpetre.

The methods of analysis are given in Vol. I., p. 471 *et seq.*

2. Potassium Chloride.

The potassium chloride used for the preparation of nitre contains at least 80 per cent. of potassium chloride and not more magnesium salts than correspond to 0·5 per cent. of magnesium chloride. For the methods of analysis, see p. 414 *et seq.*

B. Intermediate Products

The analytical methods of examination for the solid, intermediate products of the semi-refined nitre are the same as those applied to Chili saltpetre. The foreign materials, water, insoluble matter, sodium chloride, and sulphates (seldom present, or only in traces) are estimated, and the difference taken as potassium nitrate.

The analysis of the saltpetre liquors is somewhat more detailed, and primarily demands a determination of the neutrality of the liquors, *i.e.* whether they contain an excess of sodium nitrate or of potassium chloride. This necessitates an estimation of the potassium and of the nitric acid. The *potassium* is determined by accurately precipitating the sulphuric acid in 20 c.c. of the liquor in a 250 c.c. flask by means

of barium chloride, filling to the mark, and evaporating 10 c.c. of the filtrate with the requisite quantity of platinic chloride or of perchloric acid. The potassium found is calculated to potassium nitrate.

The *nitric acid* is estimated by any of the usual methods (*cf.* Vol. I., p. 473 *et seq.*), and is calculated to potassium nitrate. From the amounts of potassium and nitric acid found it is easy to determine whether the liquors contain an excess of sodium nitrate or of potassium chloride.

The determination of *iodine* in the liquors is carried out by first adding 20 c.c. of carbon disulphide to 20 c.c. of the liquor in a separating funnel of about 200 to 250 c.c. capacity, and then a small quantity of fuming nitric acid or of sulphuric acid to set free the iodine; this is extracted by shaking up with the carbon disulphide, which is separated, washed with water in a second separating funnel, and then titrated with $N/10$ sodium thiosulphate. Or the iodine in 20 c.c. of the liquor is precipitated by copper sulphate and sulphur dioxide as cuprous iodide, the precipitate washed with hot water, and the iodine determined by ferric ammonium alum and sulphuric acid.

The waste salt (sodium chloride) arising from the interaction of Chili saltpetre and potassium chloride retains some 1 to 3 per cent. of undecomposed potassium chloride and small quantities of potassium nitrate (0·25 to 0·75 per cent.), which are not removed by further washing. The potassium is determined in the usual manner by means of platinic chloride or perchloric acid. For the determination of the nitric acid, 50 g. of the waste salt is dissolved and made up to 500 c.c., and 50 c.c. of the solution (= 5 g. of the salt) used for the determination.

C. Final Product (Nitre)

The refined nitre should be free from all impurities except a small proportion of chloride. The content of sodium chloride is usually guaranteed less than 0·003 per cent. The moisture should not be above 0·25 per cent.

The nitre is tested as follows :—

Moisture. Ten g. of nitre is dried at 120° to 130° for two hours.

Chlorine. One hundred g. of nitre is dissolved in water, silver nitrate added, and the precipitate either weighed or the cloudiness compared with that produced on precipitating a standard sodium chloride solution with silver nitrate, using a nephelometer.

Insoluble impurities, *sulphates*, *calcium*, and *magnesium* are determined by the usual methods; *sodium* with potassium metantimonate. Not less than 100 g. of nitre is taken for each determination.

Any small content of *Perchlorate* (guaranteed as from 0·1 to 0·5 per

cent. at the maximum) is determined according to one of the methods given under Chili saltpetre (Vol. I., p. 484).

Potassium chlorate. Ten g. of the finely ground nitre is stirred with 20 to 25 c.c. of pure concentrated sulphuric acid in a porcelain dish cooled with water. The acid should remain absolutely colourless and show no yellow coloration.

Iodine. Small quantities of iodine compounds which may sometimes be present, are recognised by the so-called vapour test. Three g. of the substance to be tested is placed in a dry, perfectly clean test-tube, 14 to 15 mm. in diameter and 135 to 140 mm. long. Any substance sticking to the walls of the tube must be removed as completely as possible by a spill of filter paper. The test-tube is closed by a rubber stopper with one hole, through which a glass rod is inserted, fitted at the end with a hook of platinum wire. A strip of filter paper 2 cm. long by 1 cm. broad, the upper half of which is moistened with a solution of one part of chemically pure glycerine in one part of water, is attached to the hook, and suspended so that the bottom edge is 40 mm. above the substance. The test-tube is then placed in a water-bath at 71° to 72°; the temperature must be kept constant during the whole of the experiment. The test is finished after the recognised time of heating is completed, or after the characteristic coloration of the test paper has appeared, a faint yellow mark at the junction of the dry and moistened portions of the paper. On allowing the test-tube to remain longer in the water-bath, the faint yellow colour passes gradually through brown to a deep brown. Care must be taken to keep the water-bath filled above the level of the paper.

III.—POTASSIUM CARBONATE

A. Raw Materials

1. Potassium Chloride.[1]

Potassium chloride from beet ashes contains fairly large quantities of sulphate and some carbonate. The potassium, chlorine, sulphuric acid, and alkalinity are determined and the quantities of the several constituents calculated from these determinations.

In sulphate recovered from beet ashes, which contains potassium chloride and potassium and sodium carbonates, the several constituents are determined in a similar manner by determining the total alkali, sulphuric acid, chlorine, and potassium. The chlorine and sulphuric acid are calculated to potassium chloride and sulphate, the potassium

[1] *Cf. ante*, p. 414.

contained in these salts deducted from the total potassium, and the remaining potassium taken as potassium carbonate; the difference between the alkali corresponding to the potassium carbonate and the total alkali is calculated as sodium carbonate.

2. Beet Ashes.

On account of the deliquescence of beet ashes, the sample is ground in a warm mortar.

Moisture. Six to 10 g. of the powdered sample is placed between a previously weighed pair of ground watch-glasses, the glasses with sample accurately weighed, and dried at 140° till constant.

Insoluble matter. For the determination of the matter insoluble in water and the inorganic residue left after lixiviation, 20 g. of the powdered substance is weighed quickly but accurately on a clock-glass, transferred carefully into a large beaker or deep porcelain dish containing 150 c.c. of hot water, boiled and kept hot for fifteen minutes with continual agitation. The solution is filtered hot into a 500 c.c. flask, through a filter paper previously dried at 120° and weighed. A further 120 c.c. of boiling water is added to the residue, the whole again boiled and the solution decanted through the filter paper. The residue is then brought on to the paper, washed with boiling water till the total filtrate and washings are nearly up to the 500 c.c. mark of the flask, or till the filtrate commences to run through milky; the residue and paper are dried at 120°, placed between the ground clock-glasses whilst hot, allowed to cool in a desiccator, and weighed. The gain in weight gives the total matter insoluble in water. After weighing, the residue is detached from the paper and gently ignited in a large platinum dish till all the carbonaceous matter is completely ashed; the filter paper is ignited apart in the same dish. The residue remaining in the dish is the inorganic lixiviation residue, and the loss on ignition the organic matter.

The cooled filtrate (the beet ash solution) is made up to exactly 500 c.c. with distilled water, and serves for the subsequent determinations.

Alkali salts. Twenty-five c.c. of the solution (corresponding to 1 g. of beet ashes) is pipetted off into each of four small porcelain dishes and each weighed, together with a small glass rod. The solutions are evaporated to dryness on the water-bath, being stirred continually with the glass rods, the dishes covered with previously warmed watch-glasses, ignited over a free flame, allowed to cool in a desiccator, and weighed. The increase in weight gives the total alkali, the mean of the four determinations being taken as the result. The residues so obtained are used for determining the alkalinity, the potassium chloride, and the total potassium.

Alkalinity and Potassium chloride. The contents of one of the dishes (= 1 g. of beet ashes) are dissolved in cold water, washed into a beaker, and titrated with normal nitric acid, using methyl orange as indicator. The number of c.c. used multiplied by 6·910 gives the percentage alkalinity, expressed as K_2CO_3.

The neutralised solution is heated to boiling to drive off any hydrocyanic acid, and after cooling titrated with $N/10$ silver nitrate, a few drops of potassium chromate being added as indicator. The number of c.c. of silver nitrate used multiplied by 0·7460 gives the percentage of KCl, and multiplied by 0·6910 the corresponding percentage of K_2CO_3.

Potassium sulphate and Potassium sulphide. (*a*) *Total Potassium sulphate* (from the total sulphur content). Twenty-five c.c. of the filtrate from the "insoluble matter" (1 g. beet ashes) is diluted in a beaker with about 75 c.c. of water, excess of bromine water added, and the solution heated and kept boiling for about a quarter of an hour. The solution should contain excess of bromine after boiling. After saturating with hydrochloric acid and heating till the smell of bromine has completely disappeared, barium chloride solution, previously brought to boiling in a test-tube, is added. The number of mg. of $BaSO_4 \times 0{\cdot}7468$ gives the percentage of K_2SO_4 (the total sulphur compounds calculated as K_2SO_4), and the mg. $BaSO_4 \times 0{\cdot}5924$ the corresponding percentage of K_2CO_3.

(*b*) *Potassium sulphate.* The sulphuric acid in 25 c.c. of the solution from the "insoluble matter" (corresponding to 1 g. of beet ashes) is precipitated in the usual way (without previous addition of bromine), after addition of hydrochloric acid. The mg. $BaSO_4 \times 0{\cdot}7468$ gives the percentage of K_2SO_4 as such in the beet ashes, and the mg. $BaSO_4 \times 0{\cdot}5924$ the percentage of K_2CO_3 corresponding to the K_2SO_4.

(*c*) *Calculation of the Potassium sulphide.* The mg. of $BaSO_4$ found under (*b*) subtracted from those found under (*a*) multiplied by 0·4727 gives the percentage of K_2S, and multiplied by 0·5924 the corresponding percentage of K_2CO_3.

Potassium phosphate. Two hundred and fifty c.c. of the filtrate from the "insoluble matter" (= 10 g. of beet ashes) is acidified with nitric acid, and after addition of 10 g. of ammonium nitrate the phosphoric acid is precipitated by means of ammonium nitro-molybdate and weighed as magnesium pyrophosphate. The mg. of $Mg_2P_2O_7 \times 0{\cdot}1908$ gives the percentage of K_3PO_4, and the percentage of $K_3PO_4 \times 0{\cdot}9765$ the corresponding percentage of K_2CO_3.

Potassium carbonate. The ignited residue in one of the porcelain dishes from the "alkali salts" determination (containing the alkali salts from 1 g. of beet ashes) is washed with hot water into a 100 c.c. flask, acidified with hydrochloric acid, and precipitated with barium chloride so

as to leave a small amount of potassium sulphate unprecipitated, thus making sure of the filtrate being free from barium. After the addition of the barium chloride, and boiling for five minutes, the precipitate is allowed to settle for at least three hours. The contents of the flask are then made up to the mark, well mixed by shaking, and filtered through a dry filter paper. Twenty c.c. of the filtrate (=0·2 g. of beet ashes) is evaporated in a porcelain dish with 10 c.c. of a 10 per cent. platinic chloride solution, and treated as usual. The number of mg. of K_2PtCl_6 found $\times 0{\cdot}1416$ (or, if the perchlorate method is used, the number of mg. of $KClO_4$ multiplied by 0·4987) gives the percentage of total K_2CO_3. From this value the percentages of K_2CO_3 corresponding to the KCl, total K_2SO_4 and K_3PO_4, have to be deducted. The difference is the actual percentage of K_2CO_3 contained in the beet ashes.

Calculation of the Sodium carbonate. The percentage of K_2CO_3, KCl, total K_2SO_4 (not $K_2SO_4 + K_2S$, since in the weighed calcined alkali salts the K_2S is already converted into K_2SO_4), and K_3PO_4 are added together, and the sum (the percentage of all the potassium salts) so obtained is deducted from the percentage of alkali salts obtained in the determination of the "alkali salts," as above. The difference, alkali salts less potassium salts, gives the percentage of Na_2CO_3.

B. Intermediate Products

Carbonated Liquors.

The methods given under "Sodium carbonate," Vol. I., p. 530, are applicable.

C. Final Products and By-Products

1. Potassium Carbonate (96 to 98 per cent.).

The sample to be examined is well mixed, and ground as quickly as possible in a perfectly dry, preferably iron, mortar. It is then filled into dry bottles and immediately corked. The corks are best rendered air-tight by hot paraffin wax, since even sealing-wax does not prevent the sample absorbing a little moisture on long standing.

Moisture. Ten g. of the sample is heated in a platinum crucible till the weight is constant.

Insoluble matter. Ten g. of the carbonate is dissolved in warm water in a beaker, the insoluble matter filtered on to a small filter paper, washed with hot water, ignited, and weighed. Or the residue may be collected on a weighed filter paper and dried at 100°.

Potassium chloride. Two g., or in the case of a very pure sample 10 g., is carefully neutralised in a beaker with nitric acid, a drop of methyl orange being added to indicate neutrality, and titrated with $N/10$ silver nitrate, using potassium chromate as indicator. To obtain a sharp end-reaction, the solution to be titrated should be just alkaline rather than acid.

Potassium sulphate. Ten g. of the carbonate is dissolved in hydrochloric acid, filtered, heated to boiling, and precipitated with barium chloride.

Potassium silicate. Five g. of the sample is dissolved in water, filtered, the filtrate acidified with hydrochloric acid and evaporated to complete dryness, with stirring, in a platinum dish. The residue is taken up with hydrochloric acid and warmed, diluted with water, and the silica filtered off and determined in the usual way.

Total Alkali. Five g. of the potassium carbonate is accurately weighed, dissolved in a 500 c.c. flask, and the solution diluted to the mark. Twenty-five c.c. (=0·25 g.) is titrated in the cold with $N/10$ sulphuric acid, two drops of methyl orange (1 g. of methyl orange in 1000 c.c. of water) being added as indicator. The complete neutralisation is accurately recognised by adding the sulphuric acid drop by drop; the end-reaction is reached when the solution begins to change from yellow to bright rose colour. The sulphuric acid is accurately standardised in a similar manner against chemically pure anhydrous potassium carbonate.

Sodium carbonate. The ash is evaporated with hydrochloric acid and treated with barium chloride; this converts the carbonates into the corresponding chlorides. The sodium chloride is then determined by the method given on p. 415.

Fresenius has made use of the following methods to determine the sodium carbonate in the potassium carbonates (96 to 98 per cent. with 0·11 per cent. Na_2CO_3) produced at the Salzbergwerk Neustassfurt:—

(*a*) Fifty c.c. of the carbonate solution, corresponding to 1 g. of substance, is acidified with hydrochloric acid, and the sulphuric acid present precipitated with the calculated quantity of barium chloride. The barium sulphate is filtered off, washed, and the filtrate evaporated to dryness in a weighed platinum dish. The chlorides of the alkalis are weighed after gentle ignition. The potassium is then separated as usual with platinic chloride, the potassium platinichloride filtered off and washed, the filtrate along with the washings evaporated to dryness, the residue gently ignited in a current of hydrogen and extracted with water. The solution thus obtained is again treated with platinic chloride, and a further small quantity of potassium platinichloride separated. The filtrate and washings are again evaporated, the residue reduced, extracted with water, the solution evaporated in a

platinum dish, and the sodium chloride weighed, after gentle ignition. The sodium chloride is quite free from barium salts. The purity of the reagents used should be ascertained by carrying out a blank experiment.

(*b*) Ten g. of potassium carbonate is dissolved in water, neutralised with the calculated quantity of chemically pure tartaric acid and then an equal quantity of tartaric acid added, with stirring. After standing for some time any separated potassium hydrogen tartrate is filtered off and completely washed with a small quantity of cold water. The filtrate and washings are evaporated to a small bulk, any potassium hydrogen tartrate separating on standing for a short time, filtered off, washed with a little water, and the filtrate and washings evaporated to dryness in a platinum dish. The residue is gently ignited, dissolved in water to which a little hydrochloric acid has been added, the sulphuric acid carefully precipitated with barium chloride, and the excess of barium removed by addition of ammonium carbonate. The filtrate, together with washings, is evaporated in a platinum dish, the residue gently ignited, dissolved in water, the potassium separated with platinic chloride, and the sodium determined in the filtrate according to the method given under (*a*).

In calculating the results it is assumed that the sulphuric acid, silica, and the chlorine are combined with potassium, the sodium present being reckoned as sodium carbonate. The amount of potassium carbonate corresponding to the sodium carbonate and potassium silicate found is deducted from the total alkali, and the remainder calculated as potassium carbonate.

To control the working conditions in the course of manufacture, the alkali in a potassium carbonate is determined directly by titrating 2·5 g. with sulphuric acid. If a quick and accurate determination is desired, it is preferable to weigh out the required amount of substance for each individual determination, rather than to make up one amount to a definite volume and measure off aliquot parts of the solution for the estimation; this method possesses also the advantage that the most suitable conditions of concentration, etc., for rapid working can be chosen.

2. Impure Potassium Carbonate, Molasses Carbonate, and Beet Ash Carbonate.

These carbonates contain, as a rule, potassium phosphate in addition to the constituents mentioned above. The latter are determined by the methods described; the phosphate is an important indication of the origin of the carbonate. Other constituents that occur are potassium hydroxide and various sulphur and cyanogen compounds; these are

determined by the methods given under beet ashes (p. 422) and crude soda liquors (Vol. I., p. 527).

Phosphoric acid. Five g. of the sample is dissolved in nitric acid, the solution filtered, warmed, and precipitated with ammonium molybdate; the precipitate is then dissolved in ammonia, re-precipitated with magnesium mixture, filtered, ignited, and weighed as usual.

3. Hydrated Potassium Carbonate.

This is examined similarly to 96 to 98 per cent. potassium carbonate (*cf.* C. 1, p. 424).

PAINTS AND PIGMENTS

By R. S. MORRELL, M.A., Ph.D., F.I.C., and W. E. WORNUM, B.Sc., A.R.C.S., A.I.C.
(Messrs Mander Bros., Ltd., Wolverhampton).

THE inorganic or mineral colours comprise naturally occurring substances and artificially prepared products.

The chemical and physical tests employed in their examination, together serve to establish their genuineness and purity, and to determine the properties which are of value in their application.

The examination of inorganic colours is considerably complicated by the imperfect and confused nomenclature that still obtains in the industry, both of the pigments themselves and also of the specification of the qualities dealt with.

Apart from the composition of inorganic colours there are many technical properties of importance to the industries in which they are employed. They include the action of light, of moisture and climatic conditions, the colouring and the covering power, the transparency and miscibility, the action of vehicles including oils, water, spirit, etc. These will be referred to in connection with several of the colours dealt with in the sequel. The actual methods employed in the examination of these properties are extremely varied, and are essentially comparative in character; they comprise a number of physical tests, details of which are given in several of the books included in the bibliography appended to this section, and such obvious methods of examination and comparison as the specific enquiry under investigation may demand.

The Influence and Measurement of Particle Size in pigments has demanded considerable attention in recent years. The measurement is carried out by three main methods, viz.: screening, subsidence in liquid media and the direct method of microscopical analysis. Of these the method of screening is that at present adopted by the British Engineering Standards Association and consists generally in the following process[1]:—

A suitable weighed quantity of the pigment, previously crushed with a palette knife, is thoroughly soaked in white spirit (B.S.S., No. 245).

[1] Abstracted by permission of the British Engineering Standards Association, from B.S. specifications, No. 245, official copies of which can be obtained from the Secretary, 28 Victoria Street, S.W. 1, price 2s. 2d. post free.

As much as possible of the pigment is then washed through a 200-mesh (Institution of Mining and Metallurgy) standard screen with white spirit and the residue remaining on the screen is gently brushed with a soft camel-hair pencil and again washed with white spirit. The final residue is dried in a water oven at 95°-98° and weighed.

I. Naturally occurring White Auxiliary Colours; Adulterants and Substrata.

The naturally occurring white minerals, with few exceptions, are not employed as body pigments for painting, etc., since as oil colours they have not usually the required purity of tone or covering power. On the other hand, a few, such as chalk, gypsum, and infusorial earth are used to a large extent for the preparation of groundwork in fresco painting, in the manufacture of wallpapers and distempers, for lacquer work, in colour printing, for paper staining, and as adulterants. The purest clays, such as kaolin (China clay, white bole), are occasionally also used as pigments. Powdered heavy spar is employed extensively as a basis or adjunct in the preparation of mineral pigments. Native or, preferably, precipitated barium sulphate, in the form of powder, together with other white substances, serve for the preparation of lake pigments from coal-tar dyes. The detection of these additions and substrata in artificially prepared mineral and organic pigments, and the determination of their purity and applicability, are carried out according to the usual analytical methods. Certain kinds of clay, belonging to the group of acid silicates, have recently been used as colour substrata for combining with basic coal-tar dyes such as malachite green, brilliant green, and red and blue basic colours, for the preparation of the lime greens, lime reds, lime blues, etc., used in lime-washing, in the manufacture of wallpaper, etc. (See Lime Greens, p. 538.)

Calcium Carbonate.

(Chalk; Whiting; English White; Spanish White; Paris White.)

The technically important requirements of Paris White are purity of tone and fineness of texture. The crude quarried chalk is prepared for use as a pigment by grinding under water, when the coloured and argillaceous impurities and the coarser material are for the most part eliminated by levigation. The finest kinds of levigated whiting (*e.g.* Paris White) are pure white and contain only about 1.5 per cent. of impurities insoluble in hydrochloric acid. The degree of fineness

of the powder can be tested by elutriation[1] or by the process of screening as described above.

The grey-coloured "native chalks" approach the marly limes and marls in composition, with argillaceous constituents up to 25 per cent. The specific gravity of the various chalks is 2·2-2·5. Levigated chalk is chiefly used in distempering, for the preparation of painting grounds, and in the manufacture of wallpapers. It is not used in oil painting, for when mixed with oil it possesses too little covering power, dries very slowly and sometimes incompletely, and loses its colour, turning a dirty grey. It is used as putty when mixed with about 18 per cent. of linseed oil. It tends to be alkaline in reaction and hence it is not safe to mix it with such pigments as prussian blue, chrome yellow, etc.

The following analyses may be taken to represent the typical composition.[2]

	I.	II.
Calcium carbonate	94·79 per cent.	96·55 per cent.
Ferric oxide and alumina	...	0·20 ,,
Silica	3·03 ,,	0·90 ,,
Water	2·17 ,,	0·30 ,,
Magnesium carbonate	...	1·84 ,,

Analysis. A qualitative examination is first made; the material should contain only small quantities of insoluble matter (siliceous), iron, aluminium, sulphur, water or magnesium.

Total Soluble Lime. 0·75 g. of the pigment is weighed into a small crucible, ignited cautiously to dull redness to destroy organic matter, cooled, and transferred to a 400 c.c. beaker, using 20 c.c. of water. Fifteen c.c. of concentrated hydrochloric acid and 3 or 4 drops of concentrated nitric acid are added, the beaker is then covered, and the whole boiled until all the soluble matter is dissolved and the carbon dioxide expelled. The cover is then rinsed and removed, and about 150 c.c. of freshly boiled water added; dilute ammonia (sp. gr. 0·96) is then carefully added to the boiling liquid until a slight permanent precipitate remains, when 10 c.c. of a 10 per cent. solution of ammonium oxalate is added, with stirring, until the oxides of iron and aluminium are completely dissolved and only a slight precipitate of calcium oxalate persists. A further 200 c.c. of boiling water and sufficient saturated ammonium oxalate (20-25 c.c.) is next added, and after boiling with stirring for a few moments, the precipitate is allowed to settle, filtered on an 11-cm. filter, and

[1] Klein and Hulme, *J. Oil and Col. Chem. Assoc.*, 1920, **3**, 177; Schöne, *Z. anal. Chem.*, 1868, **7**, 29; Lowry, *J. Oil and Col. Chem. Assoc.*, 1922, **5**, 92; Klein and Parish, *ibid.*, 1924, **7**, 54; 1924, **7**, 82; see also *ibid.*, 1926, **9**, 192 and 252.

[2] See Holley and Ladd, *Analysis of Mixed Paints*, *etc.*, p. 95.

washed ten times with water in 10-15 c.c. portions. The precipitate is then washed down with hot water into the beaker in which it was originally formed, and dilute sulphuric acid (1 : 4) poured through the pierced filter, which is washed a few times with water. A further 30 c.c. of acid is added, the liquid diluted to about 250 c.c., heated to 90°, and titrated with standard potassium permanganate.[1] The temperature should not be below 60° when the end-point is reached. The result is calculated to CaO and $CaCO_3$.

Mixed Calcium and Magnesium Carbonates.[2] One g. of the finely powdered sample is weighed into a small porcelain dish and 25 c.c. of *N*/1 hydrochloric acid added, the dish being covered with a watch-glass. When effervescence has ceased the liquid is heated to boiling and, after cooling, titrated with *N*/1 sodium hydroxide, using methyl orange as indicator. As this method is a measure of the total alkalinity, the presence of calcium or magnesium in forms other than the carbonate would necessitate a complete analysis in order to determine the percentage of $CaCO_3$ and $MgCO_3$ in the sample.

Quicklime.

In estimating the utility of lime as a colour and a binding medium in lime-washing and fresco painting, analytical and physical tests are little used, as it is ordinarily slaked at once and thereby partly purified. Nevertheless the chemical analysis of the raw material is important, as its value is determined by the amount of argillaceous constituents, magnesium carbonate (dolomitic lime), silica, iron pyrites, and organic impurities present. The argillaceous constituents have less influence on the quality than any considerable quantity of magnesium carbonate, as in the slaking process they mostly sink to the bottom, whereas the burnt magnesia mixes with the lime and it then contains comparatively little plastic and dissolved calcium hydroxide, and is rendered granular, "thin," and less binding. Limestones containing a large amount of clay and, especially, of silica become "dead burnt," owing to the formation of calcium and aluminium silicates, which are decomposed only with difficulty or not at all. Limes of this nature contain a comparatively large amount of "cores" or particles consisting of calcium silicates which only become slaked after a considerable time; these are particularly objectionable when the lime is used for fresco painting, as they may cause subsequent loosening of the layers of material on which the picture is painted. According to A. W. Keim, such products also bring about changes in certain pigments, such as ultramarine, on account of silicate formation.

[1] Circular 40, Bureau of Standards, Washington.

[2] See J. W. Mellor, *Quantitative Analysis*, p. 522.

The slaking of lime certainly removes most of the objectionable matter, but at the same time a careful valuation of the lime is desirable. The chemical methods of estimating the value of lime by means of the calcimeter, and the technical methods of testing its setting properties, slaking capacity, etc., are described in the section on "Calcareous Cements," Vol. III.

Mixtures of dry slaked lime and casein find an extensive market as a basis of the so-called "cold water distempers." On addition of water, the casein is slowly dissolved by the alkali with the formation of a calcium caseinate, whereby the subsequent film becomes very hard, weather resisting, and insoluble in water.

Gypsum.

(Mineral White; Terra Alba; Light Spar; Agalite; Satin Spar.)

Ground gypsum, or native gypsum containing 2 mol. of water of crystallisation is the only form in which gypsum is used for cheapening artificially prepared inorganic pigments such as chrome yellows, ultramarines, Bremen blues, copper-arsenic colours, English reds, and natural mineral colours. Calcined gypsum cannot be used for dilution, as it separates out. It is used by paper stainers and makers of paper hangings in place of barytes because of its better body for that class of work. It is fairly soluble in water, about 1 part in 400-500, and more soluble in hydrochloric acid. Gypsum is valued almost entirely according to its hue when in the form of powder; it is seldom submitted to further technical and analytical examination. The methods of examination are as follows:[1]—

Combined Water and Moisture. One g. of the sample is heated in a covered basin porcelain crucible on an asbestos plate for fifteen minutes, then the bottom of the crucible is heated to dull redness for ten minutes over a Bunsen burner. The cover is removed and the heating continued for thirty to forty minutes at a slightly lower temperature. It is then weighed rapidly after cooling and reheated to constant weight. Combined water and moisture may also be determined by heating in an air bath at 200° to constant weight.

Insoluble matter. Two to 3 g. of the sample is boiled with 20 c.c. concentrated hydrochloric acid, a few drops of nitric acid, and about 50 c.c. of water; after evaporating to dryness, the residue is boiled repeatedly with 10 per cent. hydrochloric acid, decanting through a filter. The insoluble matter is washed with hot water, ignited and weighed. The residue is then tested for barium sulphate and the filtrate from the insoluble matter examined to determine if Al, Fe, or Mg are present in abnormal amounts. A separate portion of the sample is tested for

[1] *A.S.T.M. Standards*, 1918, p. 647.

CO_2, which may, if desired, be determined as under "Basic Carbonate of Lead" (p. 440). The presence of gypsum in pigments is detected by boiling with water and examining the filtrate.

Two samples of gypsum gave on analysis :—

	Gypsum.	Terra Alba.
Water	20·10	20·67
Calcium sulphate	76·69	76·52
Silica and barium sulphate . .	2·73	...
Silica	...	0·70
Magnesia	0·44	...
Oxide of iron and alumina . .	trace	0·67
Magnesium sulphate . . .	...	1·36
Undetermined	...	0·08

As regards the suitability of gypsum for mixing with other colours, nothing disadvantageous is known. Calcined gypsum is still sometimes used for this purpose; but the colours thicken when made up with binding materials containing water. The presence of large quantities in Venetian reds is generally due to the action of calcium carbonate on the ferrous sulphate during the ignition process in the manufacture of these pigments.

Barytes.

(Heavy Spar; Permanent White; Mineral White; Barite; Precipitated Barium Sulphate; Blanc Fixe.)

Common barytes consists of crushed heavy spar ($BaSO_4$), which has been levigated or water-floated to free it from coarser particles. When much impurity in the form of iron oxide is present, giving the barytes a yellow or reddish tint, it is bleached by treatment with hot dilute sulphuric or hydrochloric acid, the purified product being subsequently washed and dried.[1] The colour of barytes should be carefully attended to when buying, since the pigment is largely used in the dilution or "reduction" of white lead, on account of its low oil absorption. Many samples of apparently pure colour indicating freedom from iron develop yellowness after rubbing with linseed oil and allowing to stand for an hour or two, and this test is recommended when a determination of iron is not considered expedient.

Blanc Fixe, Permanent White, Process White, Constant White, Precipitated Barium Sulphate are obtained by precipitating solutions of barium salts (chloride), obtained as by-products in various industries, by sulphuric acid, sodium or magnesium sulphates or potash alum. In order to obtain the precipitate as finely divided as possible the

[1] T. M. Lowry, and L. Q. M'Hatton, *J. Oil and Col. Chem. Assoc.*, 1922, 5, 82, 92; C. A. Klein and W. Hulme, *J. Oil and Col. Chem. Assoc.*, 1920, 3, 177.

reaction should be carried out in the cold and with dilute solutions—precipitation from hot and concentrated solution tends to the production of crystalline particles and consequent grittiness of the pigment. The pulp from the filter press, containing 25 per cent. of water, is often used direct to save the expense of drying, *e.g.* as a base for precipitating lakes. When required, however, it is dried in a similar manner to barytes, and is a very fine powder of brilliant whiteness. Certain samples are liable to be imperfectly washed, when the traces of free sulphuric acid remaining may have a deleterious action on paint in which the pigment is used. The specific gravity of barytes varies from 4·5 to 4·75. The characteristic differences between blanc fixe and barytes are in the amorphous condition and finer state of subdivision, the greater oil absorption (15 against 6·9), and higher degree of opacity of the former. The inactivity and low oil absorption of barytes make it an important diluent of paints. It has no tendency to pass into colloidal solution in the medium, so that it must not be used alone with pigments of similar tendency as it may settle as a hard cake on the bottom of the container. Ordinary permanent white is in itself only applicable as a water colour and not as an oil colour, for when mixed with linseed oil it forms a lumpy mass. It loses this objectionable property, however, and can be employed as an oil colour, if it is completely dehydrated and then heated rapidly in a muffle to a bright red heat; the glowing mass is then chilled in cold water, and the mud so obtained ground, dried, and powdered.

The quality of permanent white is tested by A. Mierzinski's method[1] as follows:—A solution of 20 g. of glue in 1 litre of water is prepared, and a small quantity of the permanent white to be tested is made up with this glue solution to a consistence similar to that of the oil colour, and spread on strips of paper. The pigment, if of good quality, should adhere firmly to the paper after drying, and should not be rubbed off by moderate crumpling. If it does not withstand this test, it has not been prepared with sufficient care—*e.g.*, it has been precipitated in too coarse a condition, or in too acid solution, or both.

Uses. Although permanent white is one of the most unalterable pigments, it cannot compete as a body colour with other white pigments on account of its comparatively low covering power in oil vehicles. It is occasionally employed together with native heavy spar for adulterating and cheapening deep-coloured pigments, and more frequently for rendering transparent mineral colours, such as Paris blue, "warm" chrome oxide green, etc., fit for use as body colours and paints (*cf.* mineral blue, permanent greens, Victoria greens). It is employed extensively in the preparation of pigment lakes from coal-tar dyes, or more correctly for the conversion of these pigments into paints

[1] *Die Erd.- Mineral- und Lackfarben*, 1881, p. 375.

and printing colours of relatively high covering power. For this purpose it is either mixed in the form of paste with the precipitated pigments, and the mixture ground, or else it is precipitated simultaneously with the dye. Permanent white is not then an adulterant, but the substratum necessary for the attainment of the optical and other effects required. It is the recognised standard for reducing or diluting white lead in the trade. Although regarded as an adulterant a moderate proportion of barytes is an improvement to many paints, because the crystalline nature of the particles offer a good surface for repainting, whilst films of paint containing barytes suffer less contraction as they age than those of pure white lead. The greater covering power of permanent white compared with that of powdered heavy spar depends on its micro-crystalline structure. As far as investigations have gone up to the present, heavy spar and precipitated barium sulphate appear to exercise little or no detrimental effect on the permanence of coloured pigments in light and air.

Analysis. The sample is examined microscopically to determine uniformity of grinding, size, and angularity of particles, crystalline or amorphous form. The sample should contain at least 95 per cent. $BaSO_4$.

Loss on ignition. One g. of the sample is ignited for thirty minutes. The loss may be due to organic matter, moisture, combined water and carbon dioxide (also sulphur dioxide from gypsum, if present). If the loss is appreciable, the sample should be tested for carbon dioxide.

Soluble and Insoluble Matter. One g. is boiled with hydrochloric acid (1 : 3) and the insoluble matter is filtered off, washed with hot water, ignited and weighed. This may be treated with sulphuric and hydrofluoric acids in the usual manner for silica. In the absence of Al_2O_3 (from silicates) the residue is considered as $BaSO_4$. The filtrate from the insoluble matter is examined qualitatively for Al, Fe, Ca, Mg, SO_3, and a separate portion of the sample for CO_2.[1]

The following analyses show the general composition:—

Barium sulphate	98·53	96·0
Ferric oxide	0·01	0·2
Silica	0·50	0·5
Alumina	0·96	0·5
Calcium carbonate	...	1·5
Magnesium carbonate	...	0·3

White Clays.

(China Clays; Kaolin; Pipeclay; White Bole; Porcelain Earth.)

China clay is a hydrated aluminium silicate, approximately $Al_2O_3 2SiO_2 2H_2O$. Kaolin occurs as a disintegration product of the granite rocks of Cornwall. On account of its high oil absorption

[1] *A.S.T.M. Standards*, 1918, p. 647.

and transparency it is of little value as a pigment in oil paints, nevertheless it remains in good suspension in oil and inhibits the settlement of other pigments, *e.g.* barytes, red lead, etc. It is principally used as a pigment in water paints or distempers as its stability of suspension is increased in the presence of alkalis. China clay also finds application as a base for the precipitation thereon of coal-tar colours intended for use in transparent oil pigments for printing inks and water paints.

A microscopic examination is of great value, showing silica as small sharp particles, China clay to be tabloid in appearance, and asbestine to consist of long, fibrous, rod-like particles. Certain varieties of acid clay which occur near the Rhine, in Hesse and in Saxony, are not only compatible with dyes, but increase the permanence in light of the latter to such an extent, that these become serviceable only in this form of combination. (See Terre verte and Lime greens, pp. 536 *et seq.*).

The following are typical analyses :—

	Cornwall.	China.	French.	Dartmoor.
SiO_2	46·78	50·50	48·37	47·20
Al_2O_3	39·6	33·76	34·95	38·80
H_2O	13·16	11·22	12·62	12·00
K_2O	0·12	1·90	2·4	1·76
Fe_2O_3	0·09	1·80	1·26	0·27
CaO	0·07	0·04	...	0·24
MgO	...	0·80	...	...

(Hurst and Heaton, p. 140.)

Asbestine.

This pigment is asbestos in a state of fine powder. It has no body and is only suitable for giving a "tooth" to other pigments and as an adulterant for cheap paints. A typical analysis is :—

SiO_2 . .	46·3	Al_2O_3 . .	11·5	MnO . .	0·4
MgO . .	19·0	Fe_2O_3 . .	3·5	H_2O . .	2·2
CaO . .	14·0				

A qualitative analysis of China clay to determine if it is essentially hydrous aluminium silicate is generally the only chemical test necessary. Colour, fineness, etc., are more important than composition. Asbestine is tested qualitatively to prove that the material is as represented. It should be examined under the microscope to note whether it is fibrous or talcose and whether silica or China clay are admixed. Samples of known origin should be used as a guide for comparison.[1]

[1] *A.S.T.M. Standards*, 1918, p. 648.

Silica or Silex.

Silica or silex should be practically pure SiO_2. A qualitative examination will suffice in most cases, together with a determination of the loss on treating 1 g. of the sample with sulphuric and hydrofluoric acids in the usual manner.

II. White Pigments.

White Leads.

(Kremnitz White; Flake White; Pearl White.)

The chemical composition and optical properties of white lead described in most books refer to the so-called "chamber white lead" as prepared according to the old Stack or Dutch and Creed or German processes. These qualities have approximately the composition of a basic lead carbonate, $2PbCO_3 + Pb(OH)_2$, and contain on an average 1-2·5 per cent. of water, 83·5-87 per cent. of lead oxide, and 11-13 per cent. of carbon dioxide. On the other hand, those kinds prepared by the French precipitation process are said to consist almost entirely of neutral lead carbonate. The modern idea of "white lead" is therefore capable, from either the chemical or the optical point of view, of more than one interpretation. As a matter of fact, the covering power of different qualities of white lead varies considerably.

If the composition of chamber white leads is considered in the physical (optical) rather than in the chemical sense, it is the lead hydroxide, since it is amorphous, which is chiefly responsible for the covering power possessed by these products. This agrees with the fact that the French precipitated white leads being crystalline, have less covering power.

Salmonys[1] and G. Hauser[2] have shown, however, that precipitated white lead, that is, approximately neutral lead carbonate, can also be obtained in the amorphous state, and then possesses even better covering power than chamber white lead.[3] Other views on the composition of white lead have been put forward by L. Falk.[4]

For the preparation of white lead the purest possible soft lead must be employed. A lead which contains about 0·003 per cent. zinc, 0·003 per cent. iron, 0·005 per cent. antimony, 0·0006-0·0008 per cent. silver, and traces of copper, is suitable for the manufacture. Bismuth is not only non-injurious, but favours the oxidation of the lead, furnishing an

[1] *Chem. Zeit.*, 1907, 31, 955. [2] *Farben-Zeit.*, 1910, 16, 2475.

[3] *Cf.* Gebr. Hezl and A. Wultze, Charlottenburg: A process for the preparation of a white pigment consisting of normal lead carbonate. Ger. Pat. 174024 (1904).

[4] *Chem. Zeit.*, 1910, 34, 567; *J. Soc. Chem. Ind.*, 1910, 29, 769; *cf.* also, H. Hof, *Chem. Zeit.*, 1910, 34, 784.

excellent product of great whiteness and covering power. American soft lead contains about 0·75 to 1·0 per cent. of bismuth and 0·0002 per cent. of silver. If the lead used in the Dutch process is too hard for the manufacture of white lead, and acetic vapours are only allowed to act on it for the usual length of time, which is then too short, red oxides are formed.

Copper and iron in the lead are detrimental to the manufacture of white lead. These metals are estimated colorimetrically by Neujean's method[1] as follows:—20 g. of lead (40 g. if very pure, 10 g. if very impure) is dissolved in dilute nitric acid, and the lead precipitated as sulphate by sulphuric acid; the solution is filtered or decanted off, evaporated to a small bulk, and one half treated with potassium thiocyanate and the other half with excess of ammonia; the colorations so obtained are compared with standard colorations preserved in sealed tubes, and containing known amounts of iron and copper respectively. The injurious effect of silver has been examined by Krämer and Bannow,[2] who state that it is the cause of the formation of the red coloration referred to above.

Even Dutch white lead sometimes exhibits this peculiar red cast which may be due to a compound approximating to lead suboxide, or to the presence of silver, and is a result of faulty preparation (lack of carbon dioxide, insufficiently long action of acetic acid on the lead). This colour does not always disappear completely during the lixiviation process. In general, chamber white lead possesses a more pronounced yellow cast than precipitated white lead, and is therefore frequently corrected with ultramarine.

Pfund[3] uses a 1 per cent. solution of mercuric chloride to determine the degree of neutralisation in the preparation of neutral lead acetate by the French process. If a solution of crystallised lead acetate of any concentration and temperature is treated with about an equal volume of the mercuric chloride solution, the mixture remains quite clear. If, however, a trace of litharge is dissolved in the lead solution or a drop of basic lead acetate added, a considerable white cloud or precipitate is immediately formed on addition of the reagent. If the test is carried out by gradually adding the mercuric chloride solution drop by drop to a small portion of the liquid and shaking, a permanent turbidity is obtained which is formed the more rapidly the further the liquor is from the neutral point. A warm liquid which becomes cloudy on the addition of the first drop is strongly alkaline; when this takes place at about the sixth drop, the liquid is less alkaline. If it remains clear when half its own volume of the solution has been added, it will not become cloudy on addition of any further quantity—that is, it

[1] *Chem. Zentr.*, 1870, p. 642; *cf.* C. R. Hardy, *Chem. News*, 1920, **120**, 256.
[2] *Cf.* "Commercial Lead," p. 236. [3] *Dingl. polyt. J.*, 1875, **216**, 336.

contains only neutral acetate. The test is most reliable when equal volumes are used and the mercuric chloride solution is run in from a burette. The acetate solution is removed from the vessels by means of a brass cock at some distance from the bottom, and about 1 c.c. is filtered directly into a test glass. Since, in the French process, neutral acetate is regenerated simultaneously with the precipitation of the white lead by carbon dioxide, it is only necessary to prepare it once.

Commercial Qualities of Pure White Lead.—Kremnitz White is a very hard, pure, chamber white lead which is mixed with thin gum, pressed into square clay moulds, and dried. It has a smooth, vitreous fracture and was made originally in Klagenfurt.

Flake White is a variety of chamber white lead for which there was formerly considerable demand. It is obtained in flaky pieces by beating the lead plates. Its genuineness can therefore be recognised by its form.

Pearl White is white lead which has been tinted with Paris blue, indigo, or possibly with blue coal-tar colours. Bismuth oxychloride is also known as Pearl White.

Adulterated Qualities of White Lead.—Since technically pure white lead is too expensive for many industrial purposes, it is treated with white "fillers." The substances chiefly employed are heavy spar and blanc fixe (permanent white), also lead sulphate, zinc white, gypsum, China clay, whiting, clay, bone ash, etc. As long as these adulterated qualities are described as such, no objection can be made against them. It must be taken for granted that the comparatively low covering power of these qualities is known.

Two methods are in use for denoting these products: special names, or distinguishing appendices (numbers or letters) to the name "white lead." Included in this group are the commercial varieties:—*Venetian white*, which contains equal parts of white lead and heavy spar or "blanc fixe"; *Hamburg white*, which consists of 1 part of white lead and 2 parts of heavy spar; and *Dutch white*, which contains 1 part of white lead and 3 parts of heavy spar. According to the second method of designation the technically pure pigment is described as white lead "pure," and the adulterated varieties are denoted by numerals I., II., III., or 1st, 2nd, etc.

The Analysis of White Lead.

1. *Detection and Estimation of Additions and Impurities.*[1]—Five g. of the sample are treated in a tall 200 c.c. beaker with about 20 c.c. of dilute nitric acid (sp. gr. 1·2) followed by 20 c.c. distilled water, with gentle warming on a steam or sand bath. When solution is complete the contents of the beaker are diluted to about 150 c.c. and filtered

[1] Fox and Bowles, *The Analysis of Pigments, Paints and Varnishes*, p. 14.

through an ashless filter paper into a 250 c.c. graduated flask. The insoluble residue is washed free from lead, transferred to a tared porcelain crucible, dried, ignited and weighed. The residue may contain the sulphates of barium, calcium and lead, china clay or asbestine, which, if necessary, may be separated by the usual methods. Pure concentrated sulphuric acid is added drop by drop to the combined filtrates in the graduated flask until no further precipitation of lead sulphate occurs. The flask is then cooled, filled to the graduated mark with distilled water and well shaken. After allowing the precipitate to subside, 200 c.c. of the clear supernatant liquid is syphoned off into a tall 300 c.c. beaker and evaporated until sulphuric acid fumes are evolved, when any lead sulphate precipitated after dilution is filtered off, washed and rejected. The impurities are thus concentrated in a small bulk of dilute sulphuric acid. The solution is saturated with sulphuretted hydrogen and any precipitate is filtered off, washed free from acid and extracted on the filter paper with a little dilute sodium sulphide. Any antimony or tin thus dissolved is reprecipitated by faintly acidifying with hydrochloric acid and passing sulphuretted hydrogen gas. After a short digestion in a warm place, the precipitate is filtered off, ignited and weighed as oxide. The residue from the sodium sulphide treatment is dissolved in nitric acid and bismuth, if any, removed by treatment with a little ammonium carbonate solution. Traces of copper in the filtrate may be estimated colorimetrically by comparing with a standard solution of copper (*cf.* p. 64).

The main filtrate from Group II. metals is rendered alkaline with ammonia, a few drops of ammonium sulphide solution added, and the precipitated iron and zinc sulphides are filtered off, ignited direct to oxides and weighed. The proportion of iron present in the ignited precipitates may be determined by dissolving in hydrochloric acid and titrating with titanous chloride solution. The filtrate from above is transferred to a porcelain basin, evaporated to dryness and ignited to drive off ammonium salts. The residue, which consists of sulphates of calcium, magnesium and alkalis is then taken up in a little water, transferred to a platinum basin, evaporated, reignited and weighed.

2. *Estimation of Carbon Dioxide.*—The covering power of *chamber* white lead increases with the quantity of hydroxide, and decreases as the quantity of lead carbonate increases, so that an estimation of carbon dioxide is practically an estimation of the value of the white lead; but judgment of the covering power of a sample of white lead from the content of carbon dioxide no longer holds good generally.

Weise found in :—

White lead of best quality, 11·16 per cent. CO_2.

White lead of second quality (still very good), 11·68 per cent. CO_2.

White lead of third quality (still quite serviceable), 12·28 per cent. CO_2.
Drum residue, very poor quality, 14·10 per cent. CO_2.
Abnormal products of the chambers, quite useless, 16·15 per cent. CO_2.

For the estimation of carbon dioxide a portion is finely powdered, dried at 100°, either decomposed by acid in a Schrötter or similar apparatus or determined by the volumetric method of Davis and Klein,[1] which is extensively employed as a work's method in this country, or by the gravimetric method of Fox and Bowles.[2]

In addition to the above, the determination of the *Loss on Ignition*, which is proportional to the amount of lead carbonate and water, serves for the valuation of chamber white lead. In unmixed qualities it varies between 13 and 16 per cent., and amounts on an average to 14·5 per cent. Hamberger found in three qualities of white lead 21·9, 22·79, and 22·70 per cent. of calcium carbonate respectively.[3]

3. *Estimation of Lead Acetate.*—Many older qualities of white lead, especially the "caps" and "loaves," contain small quantities of lead acetate, which originates in the manufacture and from incomplete washing, or is purposely added in order to facilitate the moulding of the "caps" and "loaves," in which forms white lead still, though only rarely, comes into the market. This addition is specially injurious when the white lead is used as an artist's colour, for even when only 1·5-2·0 per cent. is present the pigment rapidly becomes yellow in the oil. White lead with this impurity gives, when boiled with water, a solution which is rendered turbid by sulphuric acid and is coloured brownish-black by ammonium sulphide. The estimation of the acetic acid present in white lead is carried out by a modification of Thompson's method[4]: 18 g. of white lead (extracted if previously ground in oil) is placed in an ordinary 500 c.c. flask with 40 c.c. of syrupy phosphoric acid (85 per cent.) and 50 c.c. of water. The flask is heated directly, and the material distilled down to a small bulk. Steam is then passed into the flask and distillation continued until about 600 c.c. of distillate is obtained. After adding about 0·5 c.c. of phosphoric acid the distillate is transferred to a heavy-walled flask fitted with a two-hole stopper. Through one hole passes a tube with a very small capillary bore, through which a minute stream of air may be drawn in during the distillation. Through the other hole is passed a connecting bulb tube attached to a condenser. Distillation is conducted under reduced pressure, corresponding to about 150 mm. of mercury, using a conical

[1] *J. Soc. Chem. Ind.*, 1907, **26**, 848.
[2] *The Analysis of Pigments, Paints and Varnishes*, p. 13.
[3] *Pharm. Zeit.*, **43**, 806.
[4] M'Master and A. E. Goldstein, *Analyst*, 1920, **45**, 185.

filter flask as receiver and is stopped when 10 c.c. of the distillate requires only one drop of *N*/10 alkali to produce a colour change with phenolphthalein. At no time should the volume of the liquid in the distillation flask be allowed to fall much below 100 c.c., as phosphoric acid may then come over. In the method the final distillate is always obtained clear, and the results are accordingly slightly lower than by the Thompson method, which always yields cloudy distillates. It is even possible to proceed to the analysis without previously extracting the oil.

4. *Estimation of Total Lead Oxide.* (*a*) Gravimetric.—0·5 g. of the sample is dissolved in dilute nitric acid and filtered through a small ashless filter paper into a tall 200 c.c. beaker. The filter paper is washed with hot distilled water and 10 c.c. of concentrated sulphuric acid added to the combined filtrates. The beaker is now heated on a hot plate or sand bath until sulphuric acid fumes are freely evolved. Heating is continued for a further ten minutes, when the beaker is removed and allowed to cool. The acid liquid is diluted with about six volumes of distilled water, and when cool, an equal volume of alcohol is added. After standing for about an hour the contents of the beaker are filtered through a small Gooch crucible, the lead sulphate washed with dilute sulphuric acid (1 in 8) and finally with alcohol. The crucible is dried in a steam oven, placed inside a larger porcelain crucible and ignited to low red heat until the lead sulphate appears pure white. The Gooch crucible is cooled in a desiccator and weighed.

As the lead sulphate so obtained is liable to contain a little impurity, it is dissolved in a 30 per cent. solution of ammonium acetate, and the insoluble residue, should any be found, is washed with distilled water followed by alcohol, and the crucible reignited and weighed. The difference in the two weights is the amount of lead sulphate.

Should the pigment be "off colour," indicating the presence of metallic lead, a second analysis should be made by dissolving 0·5 g. of the sample in acetic acid and precipitating the sulphate as above. The percentage of metallic lead is calculated from the difference in the weights of lead sulphate thus obtained.

(*b*) Volumetric.—0·5 g. of the sample is dissolved by boiling in 10 c.c. of concentrated hydrochloric acid. After cooling the solution to 40 c.c. it is neutralised with ammonium hydroxide. Acetic acid is added until the reaction is distinctly acid, and after dilution to 200 c.c. with hot water the solution is boiled and titrated with ammonium molybdate as described below.

The solution of ammonium molybdate is made by dissolving 4·25 g. in water and diluting to a litre. To standardise the solution, 0·2 g. of

pure lead foil is dissolved in nitric acid, and after evaporating almost to dryness, 30 c.c. of water then 5 c.c. of sulphuric acid (sp. gr. 1·84) is added and the liquid filtered after cooling. The filter containing the lead sulphate is put into a flask and boiled with concentrated hydrochloric acid until disintegrated. It is then treated with 15 c.c. hydrochloric acid, 25 c.c. of water, and finally with ammonia till alkaline. After acidifying with acetic acid, the liquid is diluted to 200 c.c. with hot water, and boiled. It is then titrated with the molybdate solution, using a fresh 0·3 per cent. solution of tannin as external indicator, the end-point being shown by development of a yellow coloration. Pure PbO or $PbSO_4$ may be used in place of lead foil for standardising the solution. *Cf.* p. 230.

It should be noted that when calcium is present it forms a more or less insoluble molybdate, and the results are apt to be high. With samples containing less than 10 per cent. of lead, the lead should be precipitated as sulphate, filtered, redissolved, and titrated as in the process of standardisation.

The following method of A. N. Finn gives the total basicity of a pure white lead: 2 g. of pigment is placed in an evolution flask, a little CO_2-free water added, and the separating funnel and condenser (Knorr type) connected up; 100 c.c. of $N/4$ nitric acid is added through the funnel, finally washing down with water. The carbon dioxide is absorbed in soda-lime in the usual manner (having H_2SO_4 and $CaCl_2$ drying tubes in train) and weighed. To the solution in the evolution flask about 20 c.c. of neutral sodium sulphate solution is added, and the liquid is titrated with $N/4$ sodium hydroxide solution (carbonate free), using phenolphthalein as indicator. The carbon dioxide found is calculated to $PbCO_3$. The amount of $N/4$ acid corresponding to the carbon dioxide is calculated and deducted from the total amount of $N/4$ acid neutralised by the sample, and the difference calculated to combined water, from which $Pb(OH)_2$ is computed.

F. H. Storer[1] estimates the total lead by dissolving 2-3 g. of the sample in 100-150 c.c. of dilute hydrochloric acid at 40°-50°, and immediately introducing into the solution a bright strip of pure zinc, on which the lead separates out; the solution is decanted through a filter paper which contains a small piece of metallic zinc. The residue in the beaker, consisting of metallic lead, is quickly washed with hot water and transferred to a crucible; the lead collected on the filter paper is rinsed into a porcelain dish, and, after removal of the zinc, added to the contents of the crucible. The metal is finally dried in a current of coal gas.

E. Lenoble[2] determines hygroscopic water by drying at 100°; carbon dioxide as loss of weight after addition of nitric acid; lead

[1] *Chem. News*, 1870, 21, 137. [2] *Ann. Chim. anal.*, 1899, 4, 118; *J. Soc. Chem. Ind.*, 1899, 18, 693.

oxide, provided no other metals are present, by igniting 1 g. of white lead; acetic acid by distilling 1 g. with tartaric acid; water of combination by calculation.

Specimens of French white lead examined by G. Tissandier contained:—

	I.	II.	III.
White lead	85·25	73·17	44·33
Zinc white	...	2·12	5·30
Blanc fixe	10·12	19·50	40·25
Calcium carbonate	4·63	...	10·12
Clay	...	5·21	...

5. *The Density of White Lead.* In forming an opinion on the covering power of white lead a determination of the density is important.[1] It is carried out in a pyknometer filled with benzene or toluene.[2] Qualities of low specific gravity (great volume) have the best covering power. White lead rich in neutral carbonate, obtained according to the French method by precipitation, is coarsely crystalline, and therefore does not cover so well as the amorphous and more voluminous white lead prepared by the Dutch process. Conclusions as to the covering power of different qualities of white lead may also be drawn from the determination of the degree of fineness by the method of screening or elutriation.

6. *Behaviour in Mixtures.* White lead which is technically pure and free from lead acetate, is unaffected in mixtures with most pigments containing sulphur (ultramarines, cinnabar); for exceptions, *cf.* cadmium yellow (p. 481). The presence of lead acetate renders mixtures with ultramarines unstable. Moreover, white lead is unstable when mixed with lime, and is thus not a lime colour; it imparts an orange colour to zinc yellow, to yellow ultramarine (barium yellow) and to strontium yellow, owing to the formation of basic lead chromate (chrome orange).[3] Zinc greens are also discoloured by white lead for the same reason. So far as is known at present, white lead does not accelerate the decomposition of other inorganic and organic pigments by exposure to light even in the palest mixtures.

Uses. White lead, although poisonous and sensitive to hydrogen sulphide, is still widely used as an oil colour by artists, and also for interior and especially for exterior work, as an equal degree of covering power and atmospheric durability is not attained by substitutes. Moreover, as nowadays five-sixths of the total white lead produced comes into the market as an oil paste, the danger of white lead poisoning is considerably diminished.[4]

[1] Thompson, *Proc. Amer. Soc. Test. Mats.*, 1913, 13, 407.
[2] E. Lenoble, *loc. cit.* [3] A. Eibner, *Techn. Mitt. f. Malerei*, 1907, 23, 151.
[4] *Cf.* E. C. C. Baly, *J. Soc. Chem. Ind.*, 1912, 31, 515; also, H. E. Armstrong and C. A. Klein, *ibid.*, 1913, 32, 320.

White Lead Substitutes.

Owing to the poisonous character of white lead and its sensitivity to hydrogen sulphide, a number of white lead substitutes have been introduced. These should be free from the disadvantages attached to white lead, and should at the same time possess those properties for which it is valued. The substitutes put forward up to the present completely fulfil only the former of these two conditions. The first substitute for white lead was zinc white, which is non-poisonous and at the same time is not discoloured by hydrogen sulphide. Then followed various lead preparations, such as *Mühlhaus White* (lead sulphate); *Pattinson's White Lead* (basic lead chloride, $PbCl_2 \cdot 2Pb(OH)_2$); and *Freeman's non-poisonous White Lead*, a mixture of lead sulphate, zinc white, baryta white, and magnesium carbonate. These pigments are less poisonous than white lead and are not blackened as rapidly or as intensely by hydrogen sulphide. Their covering power is, however, very inferior to that of white lead, on account of their crystalline condition.

White lead paint dries to a rather soft surface, weathering to a chalky coat, easily absorbed. White zinc (zinc oxide) paint dries more slowly, but yields a hard, almost vitreous surface. A mixture of the two, such as 60 per cent. white lead and 40 per cent. zinc oxide, shows a material correction of qualities. For the properties of leaded zinc, see S. J. Cook, *J. Soc. Chem. Ind.*, 1919, **38**, 137T.

J. A. Singmaster and F. G. Breyer patent the preparation of a zinc lead pigment containing 65-97 per cent. zinc oxide and stated to possess the covering power, opacity, and flow of XX brand of American process zinc oxide.[1] B. Paxton[2] describes a rapid volumetric process for the analysis of basic lead sulphate.

Basic sulphate of lead is manufactured in this country by roasting galena; it is also produced as a by-product in certain processes for the manufacture of litharge. The American pigment—sublimed white lead—produced from mixed lead and zinc ores, contains besides basic lead sulphate, varying amounts of zinc oxide, sulphur dioxide, occluded or in combination, and soluble zinc sulphate.

Analysis of Zinc Lead, Leaded Zincs (Ozlo White), Basic Lead Sulphate and Sublimed White Lead.

Total Lead and Zinc.[3] 0·5 g. of the dry pigment is dissolved in 25 c.c. of hydrochloric acid (1 : 1) using a 200 c.c. beaker. When solution is complete 100 c.c. of hot distilled water is added and the solution is filtered from insoluble matter into a tall 300 c.c. beaker. The insoluble

[1] U. S. Pat. 1257136, 1918. [2] *Chem. and Met. Eng.*, 1922, **23**, 989.
[3] Fox and Bowles, *The Analysis of Pigments, Paints and Varnishes*, p. 17.

matter is washed thoroughly with hot water and, if appreciable, is ignited and weighed. Ten c.c. of pure concentrated sulphuric acid is added to the combined filtrate and washings and the beaker is heated on a hot plate until sulphuric acid fumes are evolved. The acid solution is diluted, and the lead sulphate filtered through a Gooch crucible and weighed as previously described under White Lead (p. 442). If zinc has been found present in a preliminary test, the filtrate from the lead sulphate is rendered alkaline with ammonia and filtered from any precipitate of iron. The precipitate is redissolved in hydrochloric acid and reprecipitated with ammonium chloride and ammonia, the filtrate being added to the main filtrate and the precipitate neglected. The zinc may be determined in the filtrate either gravimetrically or volumetrically as described later under zinc pigments (p. 449).

Total Sulphates other than Barium Sulphate.[1] 0.5 g. of the pigment is treated in a 400 c.c. beaker with a few drops of alcohol, followed by the addition of 10 c.c. of bromine water, 10 c.c. of hydrochloric acid (1 : 1) and 3 g. of ammonium chloride. The beaker is covered with a watch glass and the contents digested on a steam bath for five minutes, when hot distilled water is added to bring the total volume to about 200 c.c. After boiling for five minutes, any insoluble matter is filtered off and thoroughly washed with hot water (a pure pigment should be completely dissolved). The combined filtrate and washings are neutralised in a covered beaker with dry sodium carbonate, 1 g. being added in excess, and boiled for ten to fifteen minutes. The precipitate is allowed to settle, filtered and washed with hot water; it is redissolved in hydrochloric acid (1 : 1) and reprecipitated with dry sodium carbonate as above, filtered and washed with hot water. The united filtrates are acidified with hydrochloric acid, adding 1 c.c. in excess, then boiled to expel bromine, and to the clear boiling solution 15 c.c. of a 10 per cent. barium chloride solution is slowly added with stirring. The precipitate is allowed to stand on the steam bath for about one hour, filtered on a weighed Gooch crucible, washed with boiling water, dried, ignited and weighed as $BaSO_4$. The result is calculated to SO_3 (including SO_3 formed from SO_2).

Alternatively 0·5 g. of the sample may be dissolved in 25 c.c. of water, 10 c.c. of ammonia (sp. gr. 0·90) and hydrochloric acid in slight excess, then diluted to about 150 c.c. with water, and a piece of aluminium foil added which should about cover the bottom of the beaker. This is held on the bottom by means of a stirring rod. The liquid is heated gently till all lead is precipitated, and decanted through a filter, pressing the lead sponge with a flattened rod, and finally washing it with hot water. A little pure bromine water is added to the filtrate which is then boiled till the bromine is expelled.

[1] *Circular of the Bureau of Standards*, No. 85.

Fifteen c.c. of 10 per cent. barium chloride solution is added and the whole allowed to stand on the steam-bath for one hour. It is then filtered, washed with hot water, ignited and weighed as $BaSO_4$ (any $SrSO_4$ present is not decomposed in this method).

Soluble Zinc Sulphate. Two g. of the sample is heated nearly to boiling with 150 c.c. of water and 50 c.c. of 95 per cent. alcohol for thirty minutes; then filtered and washed with a mixture of alcohol and water (1 : 3). The filtrate is heated to boiling till most of the alcohol is expelled, and the SO_4 determined by the usual method. The result is calculated to $ZnSO_4$ and SO_3. If the sample contains calcium or magnesium, the lead and zinc should be separated by precipitation with hydrogen sulphide after dissolving in hydrochloric acid, making alkaline with ammonia and acid with acetic acid. The mixed sulphides are dissolved in dilute nitric acid and the lead and zinc determined as above.

Sulphur Dioxide is determined as under "Basic Sulphate of Lead" (below) or "Zinc Oxide" (p. 451).

Basic Sulphate of Lead.

Purex is a basic lead sulphate having approximately the composition $2PbSO_4 \cdot PbO$. It is said to be a very resistant paint, and to flow very readily on account of the uniformity and spherical shape of the particles.

The analysis is carried out as follows:—

Total Lead. One g. of the sample is dissolved in 100 c.c. of a mixture consisting of 125 c.c. of 80 per cent. acetic acid, 95 c.c. of ammonia (sp. gr. 0·90), and 100 c.c. of water. The solution is added while hot, and then diluted with 50 c.c. of water, boiled until the sample is dissolved, diluted to 200 c.c., and then titrated with standard ammonium molybdate solution as described under basic carbonate of lead (p. 442). The ammonium molybdate solution contains about 8·67 g. per litre and is standardised against pure lead foil, pure PbO or $PbSO_4$. (*Cf.* p. 230.)

Total Zinc. One g. of the sample is boiled with 30 c.c. of water, 4 g. of ammonium chloride, and 6 c.c. of concentrated hydrochloric acid (some lead sulphate or chloride may not dissolve). Two hundred c.c. is diluted with hot water, 2 c.c. of a saturated solution of sodium thiosulphate added, and the liquid titrated with a standard solution of potassium ferrocyanide in the usual manner.

Sulphur Dioxide. Two g. of the sample is digested with frequent stirring in 100 c.c. of freshly boiled cold water and 5 c.c. of concentrated hydrochloric acid and allowed to stand ten to fifteen minutes. An excess of *N*/100 iodine solution is then added, and the excess titrated

back with $N/100$ sodium thiosulphate, using starch indicator. The result is reported as SO_2. Blank tests are run with reagents used, or the SO_2 may be titrated directly with iodine.

Soluble Zinc Sulphate is determined as under "Zinc Lead and Leaded Zincs" (p. 447).

Pattinson's white is recognised by the fact that it dissolves in dilute nitric acid without effervescence and gives a precipitate with silver nitrate. *Antimony white* and *Titanium white* are now promising substitutes for white lead (see pp. 464, 465).

In addition, *Lithopone*, and many compositions of which the basis is chiefly lithopone mixed with white lead or zinc white, also with whiting, gypsum, magnesia and silica, have been introduced. When these substances contain white lead they cannot be described as "white lead substitutes." Many of them were given fancy names in order to disguise their composition, e.g., *Oil white*, *Light white*, *Diamond white*, *Edelweiss*, *Snow white*, *Anti-white lead*, *Albanol*, *Blenda*, *Condor*, *Fixopone*, *Nivan*, *Leukarion*, etc.

None of these substances is in the strict sense a substitute for white lead, for although they do not exhibit its defects, they do not approach it either in covering power, or in stability in oil paint for open-air work.

Zinc White.[1]

(Snow White; Chinese White.)

The introduction of zinc white as a substitute for white lead was proposed by Courtois of Dijon in 1780, and in 1786 he began to manufacture it on the large scale. In 1854 the firm of Winsor & Newton put on to the market a particularly dense zinc white under the name of *Chinese white*. Since then this name has been used to designate the purest zinc white, and this applies also to the name "*Snow white*." In 1840 the artist Leclaire tested the properties of zinc white as a pigment and found them suitable, with the result that it was soon afterwards introduced as an artists' colour. The chief grounds for this were its non-poisonous character and its permanence towards hydrogen sulphide.

The individual qualities of zinc white vary in technical purity and tone according to the purity of the ores employed for its preparation, and in density according to the temperature at which the preparation is carried out. The impurities which occur are oxides of cadmium and antimony, arsenic, lead, iron, unburnt zinc, and coal dust. The zinc white used as an artists' colour and as a paint is generally pure white or of a somewhat yellow cast (cadmium oxide). Individual

[1] Cf. *Le Blanc de Zinc et le Lithopone*, A. Souris, 1912.

qualities differ less in purity than in density, and are distinguished by a system of *sealing*, zinc white "green seal" being the whitest and most bulky quality; after this come the brands red, blue, yellow, and black seals. This method of designation, therefore, is used to indicate physical differences in the qualities of technically prepared zinc oxide.

Analysis.[1] Zinc white should dissolve completely in acetic acid without effervescence. The solution on treatment with ammonium sulphide should give a pure white precipitate, and with potassium hydroxide a precipitate of similar appearance completely soluble in excess of the reagent. If the precipitate with ammonium sulphide is grey, either iron or lead is present; if cadmium is present, the precipitate is yellowish. The amount of water present should not exceed 2-3 per cent.; it must be estimated at the lowest possible temperature. Arsenic and antimony are detected by passing hydrogen sulphide into a warm hydrochloric acid solution. It is often stated that zinc oxide absorbs carbon dioxide from the air and is converted into the basic carbonate; but this reaction does not appear to proceed to any considerable extent. Thus no great significance attaches to the statements that zinc oxide on standing in the air becomes crystalline owing to absorption of carbon dioxide, and thereby exhibits diminished covering power.[2]

Total Zinc. (*a*) Gravimetric.—One g. of the sample is dissolved in acetic acid and filtered from any insoluble matter. The acid is neutralised with ammonia, 1 or 2 drops of acetic acid are added and the hot solution is saturated with sulphuretted hydrogen. The precipitate is allowed to settle, the supernatant liquid filtered, washing by decantation and finally transferring the precipitate completely to the paper. The precipitate is then dissolved in the minimum quantity of hydrochloric acid, washed through into the same beaker and boiled to expel sulphuretted hydrogen.

The zinc may now be estimated by one of the following processes:—

(1) By precipitation as Carbonate:—Sodium carbonate solution is added to the cooled solution of zinc chloride until it becomes turbid. The solution is then heated to boiling, a drop or two of phenolphthalein solution is added, followed by a further quantity of sodium carbonate solution until just alkaline. The precipitate is filtered hot through a Gooch crucible, washed well with hot water until 2 or 3 c.c. of the filtrate leaves no residue on evaporation, dried, ignited, and weighed as zinc oxide.

[1] *A.S.T.M. Standards*, 1918, p. 643.

[2] *Cf.* "Die Surrogate in der Lack-, Firnis- und Farbenfabrikation"; also, P. Beck, "Über weisse Bleifarben und die sog. Bleiweissersatzmittel," *Chem. Ind.*, 1907, 30, 27c.

(2) By precipitation as Zinc Pyridine Thiocyanate[1]:—Zinc may be separated quantitatively from manganese, magnesium, alkalies and alkaline earths by precipitation as zinc pyridine thiocyanate, $ZnPy_2(SCN)_2$. On account of the bulkiness of the precipitate, it is not advisable to work with more than 0·2 g. of zinc oxide, but larger quantities may be used with special precautions.

0·2 g. of the pigment is dissolved in the minimum quantity of hydrochloric acid and filtered from insoluble matter. Ammonia is added to the cold solution until just neutral, using a little methyl orange as indicator. This is important and very dilute ammonia or acid should be finally used to bring the solution to the neutral point. A small excess of a concentrated solution (or solid salt) of ammonium thiocyanate is introduced, when pyridine is added with vigorous stirring a drop at a time, until 15 to 20 drops have been used. More pyridine will be required for a larger quantity of the pigment. After standing for fifteen minutes the precipitate is filtered on a paper and washed with an aqueous solution containing 0·25 per cent. each of ammonium sulphate, ammonium thiocyanate and pyridine. The precipitate is then dried, transferred to a porcelain crucible and ignited apart from the paper to zinc oxide over a strong Bunsen or Téclu burner. Should the ignited zinc oxide remain massed together it is advisable to break it down with a platinum wire to ensure that no unburnt carbon remains.

(*b*) Volumetric.[2]—In the absence of iron, manganese, or other metals yielding sparingly soluble ferrocyanides, this process can be carried out without previous precipitation of the zinc as sulphide. Lead does not interfere with the determination if present only in small quantities. The following solutions are required:—

Standard Potassium Ferrocyanide.—43·2 g. of the crystallised salt $K_4Fe(CN)_6 \cdot 3H_2O$ per litre.

Indicator.—A 15 per cent. solution of uranyl acetate or nitrate, the latter being preferable.

Standardising the Potassium Ferrocyanide Solution.—3·1 g. of pure freshly ignited zinc oxide is dissolved in 10 c.c. of concentrated hydrochloric acid and diluted to 250 c.c. in a graduated flask. Twenty-five c.c. of this solution is transferred to a conical flask and 10 c.c. of concentrated hydrochloric acid added. The acid is neutralised with ammonia and a further 3 c.c. of concentrated hydrochloric acid added. The ammonium chloride so added to the solution produces a sharper end-point. It is important that the quantity of free acid present shall be constant for all determinations, and the accuracy of the method depends on a rigid adherence to standard conditions.

[1] Spacu, *Bul. Soc. Stiinte Cluj.*, 1923, **1**, 361; *J. Chem. Soc.*, 1923, **124** (ii), 580.
[2] Fox and Bowle, *The Analysis of Pigments, Paints and Varnishes*, p. 26.

The contents of the flask are diluted to 200 c.c. and heated just to boiling. Twenty-four c.c. of the potassium ferrocyanide solution is then run in, when the bluish-white precipitate becomes flocculent. The ferrocyanide solution is then added drop by drop, shaking well all the while, the precipitate meanwhile becoming pale cream in colour and losing its flocculent appearance. This occurs when the titration is within 1 c.c. of the end-point. At this stage two drops of the solution are placed on a white porcelain plate in contact with the first of a series of drops of the indicator. The burette reading is noted, a further addition of the ferrocyanide solution made and the solution tested after each reading of the burette, until a brown coloration due to uranyl ferrocyanide develops in the test drops. Since the colour takes about one minute to develop, the burette reading corresponding with the first drop which develops the brown coloration is taken as the end-point. A blank determination should be made in order to correct for the amount of ferrocyanide solution necessary to colour the indicator. This is usually about 0·2 c.c. Each c.c. of the standard potassium ferrocyanide solution should be equivalent to 0·01 of zinc.

In the titration of a solution containing an unknown quantity of zinc the progress of the reaction may be determined by the change in the appearance of the precipitate or a preliminary titration may be first made. Alternatively, the solution may be divided into two halves, the quantity of ferrocyanide solution added to the second half being just short of that required by the first, when the titration is completed by the addition of the ferrocyanide solution drop by drop.

Total Soluble Sulphur. Ten g. of the sample is moistened with water, a few drops of bromine added and then concentrated hydrochloric acid. It is boiled to expel bromine, any insoluble matter filtered off and washed with water, the filtrate made alkaline with ammonia, then just slightly acid with hydrochloric acid, heated to boiling and about 15 c.c. of hot barium chloride solution added. After allowing to stand several hours (overnight), the sample is filtered on a Gooch crucible, washed well with hot water, dried, ignited for five minutes, and weighed as $BaSO_4$. The result is calculated to sulphur.

Sulphur Dioxide. Five g. of the sample is mixed with 50 c.c. of warm (freshly boiled and partly cooled) water to an emulsion, poured into a stoppered flask containing 18 c.c. of hydrochloric acid, and exactly 25 c.c. of $N/10$ iodine solution; then the flask is stoppered and shaken until all the oxide is dissolved, and the excess of iodine titrated as rapidly as possible with $N/10$ sodium thiosulphate solution. The result is calculated to SO_2.

Soluble Zinc Sulphate is determined as on p. 447.

Fastness to Light. H. F. Link[1] discovered that zinc oxide becomes darker in the light. According to T. L. Phipson,[2] J. Cowley,[3] and J. B. Orr,[4] many qualities of zinc white are sensitive to light. Mitscherlich[5] showed that crystals of zinc selenate change their crystalline form on exposure to light. It was, however, the discovery of the sensitiveness of lithopone to light that again directed attention to this property of zinc compounds. It is accordingly necessary to test the commercial qualities of zinc white in this respect, although in these the amount of darkening does not appear to be very great.

The Incompatibility of Zinc White in Mixtures with other Pigments. On this subject there are only isolated statements, such as those of Russell and Abney,[6] according to which an addition of Chinese white in colour washes spread on test papers heated in sealed tubes brought about distinct changes in the colours. A. Eibner[7] ascertained that zinc white had considerable action on most inorganic pigments in the light, and brought about surprising rapid changes in all organic pigments. These phenomena are particularly marked when gum arabic is used as a vehicle. Under these conditions zinc white causes alteration in the chrome yellows, chrome oranges, chrome reds, chrome greens, zinc yellow, yellow ultramarine, zinc greens, cadmium yellows, cadmium red, cobalt yellow, the cinnabars, ultramarines, and Guignet greens. The cobalt violets, cobalt blues and cobalt greens appear to be almost entirely unchanged. Paris blues and Turnbull blues are decolorised with extraordinary rapidity; this light reaction is, however, reversible, like that of the unmixed Paris blues. That this accelerated action is due to the zinc white as such, and is not induced by the degree of dilution of the various pigments in question, is shown by the fact that equal percentage mixtures of the same pigments with lithopone, whiting, white lead and blanc fixe, exposed to light for the same length of time, undergo either only very slight alteration or none at all.

Further experiments show that zinc carbonate, hydrated zinc sulphide, and cadmium carbonate, also alter many pigments on exposure to light (*cf.* cadmium yellow).

Other less used artificial white pigments are: *Satin white,* which consists of a mixture of calcium sulphate and aluminium sulphate, *Manganese white, Strontium white, Tin white, Bismuth white,* and *Tungsten white.*

[1] *Über die Natur des Lichtes*, Petersburg, 1808; cf. *Geschichte der Photographie*, by Eder, p. 109.
[2] *Chem. News*, 1881, 43, 283, and 1881, 44, 73.
[3] *Ibid.*, 1881, 44, 51 and 167.
[4] *Ibid.*, 1881, 44, 12.
[5] *Pogg. Ann.*, 6, 19, and 12, 144 (from *Photochemie*, by Eder, pp. 153 and 124).
[6] *Cf.* A. H. Church, *The Chemistry of Paints and Painting*, p. 340.
[7] *Farben-Zeit.*, 1911, 16, 1754.

Lithopone.[1]

(Charlton White; Zinc Sulphide White; Sulphide White; Enamel White; Griffith's patent Zinc White; Knight's patent Zinc White; Orr's White; Ponolith; Jersey Lily White; Becton White.)

The name "Lithopone," used in the widest sense, is applied to mixtures of zinc sulphide and zinc oxide with sulphates of the alkaline earths, particularly barium sulphate. Orr first made zinc sulphide from barium sulphide and zinc chloride, and later prepared a mixture of zinc sulphide and strontium sulphate. Griffith's zinc white (1877) is a mixture of zinc sulphide and calcium or barium sulphate.

Meissner[2] prepared mixtures of zinc white and blanc fixe. The white pigment (zinc anhydride, zinc baryta) prepared by Alberti[3] is of similar composition. The commercial products now known as lithopones are essentially mixtures of precipitated zinc sulphide and barium sulphate. In order to attain the necessary covering power for such a white lead substitute, each of the constituents should possess as good covering power as white lead itself; this, however, is not the case. The optical principle adopted in the preparation of lithopone for the purpose of securing the greatest possible covering power is as follows. An intimate mixture of two pigments of different refractive power is prepared in the amorphous form—not by mixing the dry constituents, but by precipitation—so that the differences of refraction of both towards air are as great as possible. Diffuse reflection of light as well as total reflection then takes place at the bounding surfaces of the grains more easily than would be possible in the case of a single pigment.

Mixtures of blanc fixe and zinc sulphide prepared by precipitation do not, however, possess sufficient covering power. The density of the pigment must therefore be increased by heating to redness, after which it is chilled in water in order to ensure the necessary fine state of division (fineness of grain). In the course of this process any free sulphur present in the precipitated mixture is burnt away and the zinc sulphide dehydrated. Meissner converted zinc sulphide completely into zinc oxide at white heat by means of high-pressure steam. At the present time the calcination of the pigment is no longer carried to the point at which the zinc sulphide is completely oxidised. Although the calcination process in the manufacture of lithopone results in the greatest possible covering power there are disadvantages connected with it. Part of the zinc sulphide is burnt to zinc oxy-sulphide, basic and neutral zinc sulphate and zinc oxide. Lithopone

[1] Cf. *Le Blanc de Zinc et le Lithopone*, A. Souris, 1912.
[2] Ger. Pat. Nos. 4626 and 5926. [3] Ger. Pat. No. 80751.

prepared from zinc chloride solutions produces zinc oxychloride. These constituents appear to be partly responsible for the want of permanence in light exhibited by the lithopones.

Lithopones prepared from pure materials (free from cadmium) possess a purer white tone than "chamber" white lead: they are non-poisonous and are not affected by hydrogen sulphide. When ground in oil they possess covering power equal to that of French white lead.[1] Many qualities are not pure white but greyish or more or less yellow, and contain carbon, iron, alumina, or cadmium oxide as impurities.

The more valuable and better covering component of these pigments is the anhydrous zinc sulphide, and they are, therefore, sold according to their content of this constituent.[2] With lithopone, as with zinc white, designation by "sealing" is used. In this case, however, the "sealing" does not refer to purely physical differences in quality, but to the percentage of zinc sulphide, which forms the standard of value. A fixed amount of zinc sulphide corresponds to each seal, viz.:—

Green seal . . .	33 per cent. ZnS and upwards	
Red seal . . .	30 „ „	(1 per cent. latitude)
White seal . . .	26 „ „	(1 „ „)
Blue seal . . .	22 „ „	(1 „ „)
Yellow seal . . .	15 „ „	(1 „ „)

In general, however, the sealing appears to be arbitrary, for a product containing 30 per cent. ZnS is sold from one factory as "red seal brand," and from another as "green seal," so that in this case, as in that of many other pigments, it is desirable to set up a series of standards. The different brands of lithopone are naturally of unequal covering power on account of the varying proportions of the two constituents.

A. H. Pfund has designed an instrument named the "cryptometer" for determining the hiding power of pigments and paints, the principle of which appears free from objection and the application simple and rapid.[3] He has also recently devised an instrument which shows every promise of becoming an almost indispensable piece of apparatus to the paint technologist.[4] In this new colorimeter for white pigments the principle of multiple reflections is adopted in order to accentuate departure from white and a piece of ground optical glass is used as a non-selective reflecting surface. In order to obviate the necessity of standardising a source of white light, the colour characteristics of the

[1] *Cf.* J. F. Sacher, *Farben-Zeit.*, 1910, **15**, 1543; 1911, **16**, 542; and Meister, *ibid.*, 1910, **15**, 1652.

[2] *Cf.* E. Kochs and E. Seyfert, *Z. angew. Chem.*, 1902, **15**, 802; *J. Soc. Chem. Ind.*, 1902, **21**, 1145.

[3] *J. Franklin Inst.*, 1919, **188**, 675. [4] *Proc. Amer. Soc. Test. Mats.*, 1920, **20**, Part II., 440.

paint are given in terms of "brightness." For colours of dominant hue 460 $\mu\mu$ (blue), 550 $\mu\mu$ (green), and 625 $\mu\mu$ red respectively. In this way the colour characteristics are established and standard samples of paints may be discarded. This method of investigation shows that all "white" pigments are yellowish, though when compared with one another some may be pinkish, bluish, etc. By addition of a trace of lampblack to a zinc oxide paint, the latter becomes nearly non-selective, and whereas the "brightness" of the paint is diminished by only 3.5 per cent. its hiding power is increased by 17·5 per cent.

Analysis. In the analysis of lithopone, in addition to zinc sulphide and barium sulphate, secondary constituents dependent on the method of manufacture must be taken into account, viz.—zinc oxide, possibly zinc carbonate, zinc oxychloride, zinc oxysulphate, zinc sulphate, barium carbonate and barium sulphide.[1] Many processes embody the introduction of small quantities of certain salts — alkaline phosphates, bicarbonates and borates—which are stated to combine with metallic zinc as fast as it is formed and are thus designed to inhibit the darkening of lithopone on exposure to light. Of technical impurities lead, thallium or manganese are said to produce the swiftest and most severe discoloration. Iron, nickel or cobalt are slower in action, but complete immunity from colour change seems to be obtained only by the absence of all metallic impurities of the kind indicated.[2] Other impurities include ferric oxide, alumina, lime, magnesia, copper and carbon. A qualitative examination for the constituents mentioned should precede the quantitative analysis.[3]

I. *Estimation of Zinc.* (*a*) Gravimetric Method.—P. Drawe[4] recommends the following method:—The total amount of zinc present as sulphide, oxide, oxysulphide, etc., is first determined. For this purpose 1·0-1·5 g. of the finely powdered sample is weighed out into a beaker of about 200 c.c. capacity, agitated with 10 c.c. of hydrochloric acid (sp. gr. 1·19) and treated with 1 g. $KClO_3$ in small portions; about half of the hydrochloric acid is then evaporated off on a boiling water-bath, the solution diluted with hot water, and treated with dilute sulphuric acid in order to decrease the solubility of the barium sulphate; the solution is then decanted through a filter paper and the residue washed until the washings are no longer acid. The filtrate is heated to boiling in a porcelain dish of 500 c.c. capacity, over which an inverted funnel is placed, and, by the gradual addition of sodium carbonate solution, the acid is first neutralised, and the zinc then

[1] *Cf.* H. Wolff, *Farben-Zeit.*, 1910, **15**, 1859; also, Austin and Keane, *Analyst*, 1912, **37**, 238.

[2] Eibner, *Chem. Zeit.*, 1923, **47**, 13; *Farben-Zeit.*, 1925, **30**, 2600.

[3] *Cf.* C. Coffignier, *Bull. Soc. Chim.*, 1902, **27**, [15] 829, [18] 943; *J. Soc. Chem. Ind.*, 1902, **21**, 1146, 1377.

[4] *Z. angew. Chem.*, 1902, **15**, 174, 229, 297; *J. Soc. Chem. Ind.*, 1902, **21**, 427.

precipitated as carbonate. The precipitate is filtered off, washed, ignited, and the zinc weighed as oxide.

The estimation of the zinc present as sulphide is carried out by digesting 1-1·5 g. with 100 c.c. of 1 per cent. acetic acid in a beaker at the ordinary temperature for about half an hour, then decanting through a small filter paper, and washing well with warm water. The residue on the filter paper is then added to the residue in the beaker and the whole treated, as in the estimation of total zinc, with hydrochloric acid and potassium chlorate, etc. The zinc oxide so obtained gives the amount of zinc present as sulphide. The difference between the first and second estimations represents the amount of zinc present as oxide, carbonate, and oxysulphide.

Carbon dioxide and sulphuric acid, if present, are determined by the usual methods, and in the statement of results are taken as combined with zinc.

Barium sulphate can be estimated by direct weighing of the insoluble residue on treatment with hydrochloric acid.

E. Kochs and E. Seyfert[1] determine the zinc by precipitation with ammonium sulphide:—5 g. of lithopone heated in a half-litre flask with 100 c.c. of hydrochloric acid (sp. gr. 1·12) until all the sulphuretted hydrogen is driven off; after cooling, the flask is filled up to the mark, 100 c.c. of the filtered solution, rendered alkaline with ammonia, is treated with ammonium or sodium sulphide at 50°-70°, and the precipitated sulphide ignited and weighed as ZnO. If, on the addition of ammonia, a precipitate of iron or aluminium is formed, then the weighed oxide of zinc is dissolved in hydrochloric acid and the contained iron and aluminium determined. The zinc salts soluble in acetic acid are also determined. For this purpose 5 g. of lithopone is shaken for some time with 100 c.c. of 5 per cent. acetic acid in a 250 c.c. flask at the ordinary temperature, the solution made up to 250 c.c., filtered through a double filter paper until a clear filtrate is obtained, and the zinc precipitated in 200 c.c. of the solution. It is stated that up to 12 per cent. of zinc carbonate or oxide may be detected in many qualities of lithopone.

J. S. Remington and C. Smith[2] recommend the following method of analysis as rapid, exact, and generally applicable. The sample is first tested for salts of iron, zinc, calcium, and barium soluble in water. A separate portion is tested for barium carbonate the percentage of which is determined, if necessary, by dissolving 2 g. in 50 c.c. of dilute hydrochloric acid, filtering, and precipitating the barium soluble in hydrochloric acid with dilute sulphuric acid. For the determination of the barium sulphate and zinc sulphide 0·5 g. of the sample is

[1] *Z. angew. Chem.*, 1902, **15**, 802 ; *J. Soc. Chem. Ind.*, 1902, **21**, 1145.
[2] *Caoutchouc et Gutta-Percha*, 1909, **6**, 3259 ; *J. Soc. Chem. Ind.*, 1909, **28**, 1049.

mixed with 25 c.c. of water at 40°, 0·5 g. of bromine added, the containing flask covered with a watch-glass, and set aside for one hour during which it is occasionally agitated; 10 c.c. of concentrated hydrochloric acid is then added, the excess of bromine expelled by heat, then 25 c.c. of water added, the contents of the flask boiled and filtered, and the residual barium sulphate washed, dried, ignited, and weighed. The filtrate is precipitated with barium chloride, and the barium sulphate formed is weighed; the proportion of zinc sulphide is then calculated from the weight of barium sulphate obtained.

For the determination of the total zinc, 0·5 of the sample is treated with hydrochloric acid, boiled until all the sulphuretted hydrogen has been expelled, a little dilute sulphuric acid added, the solution again boiled, and the zinc precipitated as carbonate and weighed as oxide. This, less the weight of zinc oxide corresponding to the zinc sulphide found, gives the content of zinc oxide. Should any barium carbonate have been found, the corresponding weight of barium sulphate must be deducted from the weight of the total barium sulphate (estimated as such), and added to the weight of barium sulphate corresponding to the zinc sulphide. If salts of iron, calcium, or barium are present in the solution containing the zinc, these must be separated by ammonia and ammonium sulphide. Analyses of 12 average samples of English lithopone are given in the paper; in these the percentage of barium sulphate varies from 58·16–80·80, that of zinc sulphide from 21·54–33·92, that of zinc oxide from 0·28–3·36, and that of barium carbonate from nil to 0·98.

(*b*) Volumetric Method.—H. Amsel[1] uses the following method:—50-75 c.c. of the hydrochloric acid solution, filtered from barium sulphate, is treated with 1 c.c. of 10 per cent. ferric chloride and 20 c.c. of a 40 per cent. solution of neutral potassium tartrate; the solution is then neutralised with ammonia and boiled. If the solution is not clear more ammonia is added. The solution is then treated with a standard solution of potassium ferrocyanide until all the zinc is precipitated, this being recognised by bringing together a drop of the solution and a drop of strong acetic acid on a white porcelain plate, when a blue coloration (Prussian blue) is immediately produced. The zinc oxide or carbonate is estimated separately by extracting with 5 per cent. acetic acid. The volumetric method of estimating zinc in lithopone has the advantage of rapidity.

II. *Estimation of Zinc Sulphide by determining the Sulphur present as Sulphide.* (*a*) Gravimetric Method.—P. Porth[2] carries out this estimation according to Jannasch's method by heating the lithopone in bromine vapour and collecting the resulting sulphur bromide in dilute

[1] *Z. angew. Chem.*, 1902, **15**, 174.
[2] *Farben-Zeit.*, 1909, **14**, 1986.

hydrochloric acid. The bromine is conducted over the lithopone, contained in a boat in a glass tube, in a stream of carbon dioxide.

When barium sulphide, which occurs extremely rarely in lithopone, is present, J. F. Sacher[1] recommends that the sample be extracted with water before estimating the sulphur present as zinc sulphide. The sulphide-sulphur is then estimated by treatment with metallic tin and hydrochloric acid, and passing the evolved hydrogen sulphide into an ammoniacal hydrogen peroxide solution; the resulting sulphate is then precipitated with barium chloride. The apparatus used consists of a cylindrical glass vessel about 20 cm. long, and 2 cm. wide which can be hermetically closed by means of a glass stopper provided with a two-way cock in connection with a gas inlet and outlet tube and a funnel tube. The absorption tube containing ammoniacal hydrogen peroxide is connected to this. In carrying out the determination 1-2 g. of the purest tin, then the weighed substance (0·5–1 g.) packed in tinfoil, and over this another layer of tin are successively placed in the apparatus, concentrated hydrochloric acid is run in through the funnel, the vessel closed by turning the tap, and heated in an oil-bath to the boiling point of the hydrochloric acid. When the tin is dissolved, the decomposition vessel is connected with a hydrogen apparatus and the last traces of hydrogen sulphide driven over into the absorption vessel.

Sacher suggests a correction, in the estimation of barium sulphate in the residue, as the results come out about 0·7 per cent. too low, in consequence of partial solution of that substance in the hydrochloric acid solution of stannous chloride. He transfers the contents of the decomposition vessel to a flask and dilutes with water to 300 c.c., adds a few cubic centimetres of 10 per cent. barium chloride solution, boils, and allows to stand for a considerable time in the cold.[2]

(*b*) Volumetric Method.—H. Wolff[3] directs attention, in the first place, to the sources of error in the method of estimating the content of zinc by difference, and then to the inconvenience of precipitating zinc as sulphide and carbonate. In the latter method, when calcium is present (in lithopone "yellow seal"), it is precipitated with the zinc. He therefore recommends the precipitation of the zinc with hydrogen sulphide from a weakly acid solution. In contrast with this, the methods depending on the oxidation of sulphide-sulphur have the advantage of being direct methods, but have the disadvantage that if sulphates (zinc sulphate, gypsum) are present the estimation of the sulphuric acid already present is necessary, and they thereby become indirect. These disadvantages are overcome by iodometric

[1] *Farben-Zeit.*, 1910, **15**, 1810.
[2] Cf. *Chem. Zeit.*, 1909, **33**, 941; *J. Soc. Chem. Ind.*, 1909, **28**, 1066.
[3] *Farben-Zeit.*, 1910, **15**, 1859.

methods. Wolff removes any barium sulphide present by boiling the weighed sample with 2 per cent. acetic acid. After this treatment the lithopone is mixed with 0·5–1 g. of sodium carbonate in a 200 c.c. flask fitted with a tap-funnel and delivery tube, and hydrochloric acid is added through the funnel. The carbon dioxide evolved displaces the air and prevents oxidation of the hydrogen sulphide. On boiling, the latter is driven over into the receiver of two Peligot tubes containing respectively 50 c.c. and 2-3 c.c. of $N/14$ iodine solution. After combining the two solutions the excess of iodine is titrated back with $N/14$ thiosulphate solution. One c.c. iodine solution used corresponds to 4·873 mg. zinc sulphide. In the control estimations, or in the first estimation provided that the zinc content of the sample is known approximately, the 50 c.c. of iodine solution are divided, instead of placing the whole amount in the Peligot tubes, and a sufficient quantity is introduced into the generating flask to ensure the decomposition of some nine-tenths of the hydrogen sulphide at the moment of formation. A large excess of iodine (with lithopone "red seal" 0·3–0·4 g.) is used.

This method has the advantage of being rapidly carried out and, according to Wolff, gives more reliable results than those obtained by the double zinc estimation, especially when zinc oxychloride is present, as the latter, even with 5 per cent. acetic acid, is not dissolved without leaving a residue, but only on boiling with 10-15 per cent. acid. When either *oxychlorides* or *oxysulphates* are present, the method of double zinc estimation gives values up to 2 per cent. too low.

In order to obtain a correct idea of the composition of lithopone and especially of the distribution of the zinc, Wolff recommends that in the qualitative analysis the substance be treated successively with cold and then with hot 3 per cent. acetic acid, with hot 10 per cent. acetic acid, and finally with hydrochloric acid.

W. L. Austin and C. A. Keane[1] recommend the estimation of the total zinc volumetrically and that of the zinc sulphide indirectly by oxidising the sulphide-sulphur to sulphate. The gravimetric estimation of the zinc as carbonate is inaccurate in presence of calcium and iron, both of which are usually present, and its precipitation as sulphide is a lengthy determination. They regard the oxidation and subsequent precipitation of the sulphide-sulphur as simpler and easier to carry out than the determination of the hydrogen sulphide evolved on decomposition.

For the volumetric estimation of the zinc a method devised by A. Voigt[2] for the analysis of zinc ores and products was employed which is sufficiently accurate for the estimation, and which has the advantage that the results are not affected by the presence of iron

[1] *Analyst*, 1912, 37, 238.
[2] *Z. angew. Chem.*, 1889, 2, 307.

or calcium. For the oxidation of the sulphide-sulphur either bromine or nitric acid may be used; the former was found preferable, and the estimation is carried out on the same lines as proposed by Remington and Smith. This combination was found more rapid and adaptable than previous proposals, and sufficiently accurate for technical purposes.

The method of analysis is as follows;—Five g. of the finely ground sample is treated with concentrated hydrochloric acid and a little potassium chlorate, the whole evaporated to a small bulk on the water-bath, taken up with boiling water, and the residual barium sulphate filtered off and thoroughly washed. The filtrate is collected in a 250 c.c. graduated flask, made up to the mark, and aliquot portions taken for the estimation of the total zinc by Voigt's method (p. 298). The potassium ferrocyanide solution is made up by dissolving 46 g. of the crystallised salt in a litre of water, and is standardised by a solution of zinc chloride containing 12·4476 g. of pure zinc oxide per litre; 1 c.c. of this solution is equivalent to 0·01 g. of zinc. For the estimation, 50 c.c. of the above filtrate is taken, 10 c.c. of a solution of tartaric acid (200 g. per litre) and 10 c.c. of a solution of ferric chloride (60 g. per litre) added, the whole diluted to about 200 c.c., made just alkaline with ammonia, and titrated; the completion of the reaction is determined by adding a drop of the solution to dilute acetic acid (1 ; 3) on a pitted porcelain plate until a permanent blue colour is produced. After a preliminary estimation a sharp end-reaction is easily secured, and it is not affected by the presence of an excess of ammonia. In a series of tests made, in which the quantity of ammonia added was increased up to twice the amount necessary for neutralisation, the maximum difference in the titrations did not exceed 0·15 c.c.

For the estimation of the sulphide-sulphur, 0·5 g. of the sample is oxidised with bromine after the addition of water, hydrochloric acid added, the residual barium sulphate filtered off, and the sulphuric acid in the filtrate precipitated by barium chloride. By calculating the sulphur thus found to zinc sulphide, and subtracting its equivalent of zinc from the total zinc estimated volumetrically, the content of zinc, other than sulphide, is obtained by difference, as stated above.

The following methods are recommended by the American Society for Testing Materials.[1]

Insoluble and Total Zinc. One g. of the sample is put in a 200 c.c. beaker and 100 c.c. of concentrated hydrochloric acid added. About 1 g. of potassium chlorate is mixed and added in small portions, and the liquid then heated on a steam-bath until about half is evaporated. The sample is then diluted with water, and 5 c.c. of dilute sulphuric acid (1 : 10) added. After boiling, it is allowed to settle, the insoluble matter (which should be only barium sulphate) filtered, washed,

[1] *A.S.T.M. Standards*, 1918, p. 643.

ignited, cooled, and weighed. A qualitative examination for alumina and silica is made. The insoluble matter should then be examined under the microscope for the presence of natural crystalline barytes.[1]

The sample may also be examined direct. The filtrate from insoluble matter is made alkaline with ammonia, acidified with hydrochloric acid, 3 c.c. of hydrochloric acid added, and the liquid diluted to about 250 c.c. with water, heated nearly to boiling and then titrated with potassium ferrocyanide solution as under zinc white (p. 450). The result is calculated to Zn.

Zinc Oxide. A 4 g. sample of the lithopone is treated for four hours with 200 c.c. of 1 per cent. acetic acid at room temperature, with occasional stirring. It is then filtered by suction on a double filter paper and washed with cold water. Thirteen c.c. of concentrated ammonia is added to the clear filtrate, which is then neutralised with hydrochloric acid and 3 c.c. of concentrated hydrochloric acid added in excess. After heating to boiling it is titrated with potassium ferrocyanide, using uranium acetate solution as an outside indicator. The result is first calculated ZnO, then to Zn, and subtracted from the total Zn. The difference is calculated to ZnS. Any $ZnCO_3$ or $ZnSO_4$ is included in the ZnO.

Zinc Sulphide. 0·5 g. of the pigment is placed in an evolution glass with about 10 g. of "feathered" or mossy zinc, 50 c.c. of water is added and a stopper carrying a separating funnel and an exit tube is inserted. Fifty c.c. of concentrated hydrochloric acid is run in from the funnel, the exit tube having previously been connected to two absorption flasks in series. The first flask should contain 100 c.c. of alkaline lead nitrate solution, the second flask 50 c.c. of the same solution as a safety device.

After the acid has run into the evolution flask, it is heated slowly, and finally boiled until the first appearance of steam in the first absorption flask. The apparatus is disconnected and the lead sulphide allowed to settle. After filtering it is washed with cold water, then with hot water till the washings are neutral to litmus paper and give no reaction to lead. The lead sulphide precipitate is dissolved in hot dilute nitric acid, evaporated with sulphuric acid until fumes are evolved, and finally weighed as lead sulphate. The result is calculated from PbS or $PbSO_4$ to ZnS. The alkaline lead solution is made as follows:—Into 100 c.c. of potassium hydroxide (56 g. in 140 c.c. of water) a saturated solution of lead nitrate is poured (250 g. in 500 c.c. of water) until the precipitate ceases to redissolve. Constant stirring is necessary while mixing. About three volumes of the lead solution will be required for one of the alkali.

[1] S. Stewart, *J. Soc. Chem. Ind.*, 1920, **39**, 188T.

Instead of absorbing the sulphuretted hydrogen evolved in alkaline lead nitrate solution, a solution of 8 g. of cadmium chloride in 250 c.c. of water and 150 c.c. of ammonia (sp. gr. 0·90) may be used. The precipitate of cadmium sulphide may be filtered on a weighed Gooch crucible, washed with water containing a little ammonia, dried at 100°, and weighed. The result is calculated to ZnS. It is better to filter the cadmium sulphide on a small filter and to wash as above, then to place the filter and precipitate in a beaker and dissolve in hydrochloric acid and potassium chlorate (keeping at room temperature at first), filtering out any paper pulp or insoluble matter, making the filtrate alkaline with ammonia, acidifying with hydrochloric acid, heating to boiling, and precipitating with barium chloride in the usual manner. Finally the barium sulphate is filtered, washed, ignited, and weighed. The result is calculated to ZnS.

For very rapid work the contents of the absorption flask, after all the hydrogen sulphide has been absorbed, may be washed into a vessel with cold water and diluted to about 1 litre, acidified with concentrated hydrochloric acid and titrated with standard iodine solution, using starch indicator (the precipitate should be completely dissolved). The iodine solution is prepared by dissolving about 12·7 g. of pure resublimed iodine in 18 g. of potassium iodide in a little water and then diluting to 1 litre.

Barium Sulphate is estimated directly by weighing the residue obtained on decomposition of the lithopone with hydrochloric acid, bearing in mind the partial solubility of barium sulphate in the latter (Wolff). In addition, the estimation of moisture, which should not amount to more than 0·2-0·3 per cent., must be carried out.

Fastness to Light. The permanence of lithopone in light is practically important in view of the action of zinc white on pigments in the light. Lithopone turns grey in the light, as Phipson observed as long ago as 1880. The reaction is reversible and takes place more feebly under glass. It is therefore caused partly by ultra-violet rays.[1] The components of lithopone responsible for this lack of permanence in light do not yet appear to be definitely known. It is attributed partly to the presence of soluble salts of zinc and of other metals,[2] partly to zinc sulphide in the hydrated form,[3] and partly to zinc oxide and basic zinc salts. According to Ostwald, the grey coloration of lithopone behaves as if it proceeded from finely divided metallic zinc.[4] The causes of the discoloration of lithopone when exposed to light

[1] In opposition to this view, *cf.* O. Lehmann, *Molecularphysik*, 1888, vol. i., p. 240.

[2] Alberti, R. Steinau, Ostwald, and Brauer.

[3] de Stucklé.

[4] Church-Ostwald, *Farben und Malerei*, p. 147; and D. Scheiber, *Farbe und Lack*, 1924, No. 21, 148.

have also been investigated by W. O'Brien,[1] who also concludes that zinc is formed, and by A. Eibner.[2] Steinau[3] regards moisture as a cause of the instability of lithopone to light, and the colour change is influenced by the presence of chlorides, especially zinc chloride. For the preparation of a lithopone stable to light a well-regulated control of the chlorides content is essential.

G. Rigg[4] claims to produce a lithopone unaffected by light.

A. Eibner[5] considers that the darkening is due to the presence in the original raw materials of impurities which interact with the sulphide pigment as in the case of vermilion.

F. Bayer u. Co.[6] have patented the use of titanium oxide as a stabilising agent.

Behaviour of Lithopone in Mixtures with Pigments containing Lead. The stability of varieties of lithopone towards white lead appears to depend on their quality. A mixture of lithopone "green seal" and white lead free from acetate, mixed in water and allowed to settle, showed no change of shade in two years, whereas another mixture containing an inferior quality had become black in spots on the side exposed to the light in fourteen months. Thus even in the latter case only a reaction accelerated locally by the action of light took place. It was observed that when pale mixtures of lithopone "green seal" with coal-tar dyes were exposed to the light, the lithopone did not injure the permanence of such mixtures, but diminished it probably just as little as whiting, heavy spar, and white lead would have done. On the other hand, such mixtures have been repeatedly observed to turn grey. Thus it appears that doubtful lithopone still comes into the market.

Steinau's Sulfopone[7] is obtained by treating a solution of calcium sulphide with a solution of zinc sulphate at 44°, and heating the resulting mixture of zinc sulphide and calcium sulphate to 250°-300°.

For some years white pigments have been prepared from artificial zinc sulphide. According to J. C. A. Meyer of Lyons, this possesses even greater covering power than white lead. He found that if lead salts (about 2 per cent.) are present, the iron in zinc lyes comes down with the lead on treatment with hydrogen sulphide, and thus pure zinc solutions are obtained for precipitation with hydrogen sulphide. The precipitated zinc sulphide is then dehydrated.[8] A very finely divided and therefore good covering zinc sulphide was obtained by de Stucklé,[9]

[1] *J. Phys. Chem.*, 1915, **19**, 113; *J. Soc. Chem. Ind.*, 1915, **34**, 290.
[2] *Chem. Zeit.*, 1923, **47**, 13.
[3] *Chem. Zeit.*, 1921, **45**, 1238.
[4] U.S. Pats. 1260811 and 1260812, 1918.
[5] *Farben-Zeit.*, 1925, **30**, 2600.
[6] Ger. Pat. 383565.
[7] Ger. Pat. 74591.
[8] Ger. Pat. 192531, 25th August 1906.
[9] Ger. Pat. 167172, 19th February 1904.

by precipitation from a mixture of metallic zinc and caustic baryta solution, hydrogen being evolved at the same time; or by precipitation of zinc sulphide at the negative electrode of an electrolytic bath.[1]

Antimony Oxide.

(Timonox; Antox.)

This pigment results from the condensation of antimony oxide produced by the roasting of antimony ores (Antox, Costerfield Mines, Australia). The colour varies from pure white to dull orange, depending on the temperature of working. The pigment timonox has a sp. gr. 5·4 and produces a good paste when ground with 10 per cent. linseed oil. It has no accelerating effect as a drier, can be reduced with barytes or blended with zinc white; it is unaffected by ultra-violet light or by sulphides under ordinary conditions. It is non-poisonous,[2] and the following comparisons indicate its relative value:—

	c.c. Medium per gr. Pigment at Painting Consistency.	Total Pigment Required.	Relative Hiding Powers of Equal Masses of Pigments.	Relative Opacities of Paints of Equal Consistencies.	Volume of Paint containing 1 g. of Pigment.
Lithopone . . .	0·61	2·0	100	100	0·85
Zinc oxide . . .	1·07	2·56	87·8	53	1·25
White lead . . .	0·42	3·88	57·6	77	0·57
Timonox, "Green Star"	0·57	2·34	85·4	95·5	0·76

Timonox "Red Star" has 98·5 per cent. solubility in HCl, whilst "Green Star" has 96 per cent. solubility.

Analysis. (*a*) Gravimetric Determination of Antimony as Sb_2S_3.—0·5 g. of the pigment is boiled with 30 c.c. of hydrochloric acid (1 : 1) in a tall 200 c.c. covered beaker until solution is complete, care being taken that the liquid does not reach a temperature much above 110°, to prevent loss of antimony chloride by volatilisation. 100 c.c. of hot water is added and the liquid allowed to digest on a steam bath for a short time, when it is filtered through a 9 cm. ashless filter and washed with hot distilled water containing a little hydrochloric acid to prevent formation of the oxychloride. The cold solution is saturated with sulphuretted hydrogen, the acidity reduced by careful addition of dilute ammonia, using litmus paper as indicator, and the liquid heated to boiling, whilst the gas is again passed for about ten minutes. The orange-coloured precipitate is allowed to settle and the supernatant liquid is filtered through a Gooch crucible previously ignited at 280° in a current of CO_2. After washing the precipitate twice by decantation with water acidified with acetic acid and containing a little

[1] Ger. Pat. 167498, 14th August 1904; *cf.* also, Ger. Pat. 171872, 23rd March 1904.
[2] H. E. Clarke, *J. Oil and Col. Chem. Assoc.*, 1921, 4, 2.

hydrogen sulphide, it is transferred completely to the crucible and washing is continued until free from chloride. The crucible is dried in a steam oven, heated at a temperature of 100°-130° for two hours and finally at 280°-300° for a similar period in a stream of carbon dioxide according to the method of Henz.[1]

If tin is present, the precipitated sulphides obtained by the above method must be dissolved in hydrochloric acid, with the assistance of a crystal or two of potassium chlorate and the antimony sulphide reprecipitated in the presence of oxalic acid. The acidity of the solution containing the antimony and tin is reduced as far as possible with sodium hydroxide, and oxalic acid is then added to the hot solution until saturated. Hydrogen sulphide is passed rapidly until all the antimony has settled out and the precipitate is treated by the method already described. In very accurate work a double precipitation of the antimony sulphide is essential.

Determination of Tin.—Since the proportion of tin is not likely to exceed 1 or 2 per cent., it may be separated in the filtrate as metal by adding hydrochloric acid and a plate of clean zinc. After ten to twelve hours the tin so precipitated is carefully collected, washed and mixed with an excess of ferric chloride and a little hydrochloric acid. When solution is complete the ferrous iron is titrated with *N*/10 permanganate.

(*b*) Volumetric.—For this Mohr's method may be employed. 0·2 g. of the pigment is dissolved in hydrochloric acid and boiled for a few minutes. One g. of tartaric acid is added and the solution rendered just alkaline with sodium carbonate, finally just acid with tartaric acid. Twenty c.c. of a cold saturated solution of sodium bicarbonate is added and the solution is titrated with *N*/10 iodine solution, starch being added towards the end of the reaction. One c.c. of *N*/10 iodine =0·00607 Sb. Lead, even in relatively large quantities has no influence on the results, but tin in the lower state of oxidation, as well as arsenic and iron in more than traces, affects the process. Any arsenious oxide present in the pigment, however, is largely removed in dissolving the sample in hydrochloric acid and only the merest traces of iron would be expected in a white pigment.

Titanium Oxide.

(Titanium White.)

Titanium oxide is obtained from a variety of ilmenite (Egersund, Norway). The ore is freed from associated minerals and the concentrate, containing 47·5 per cent. titanium oxide, is finely powdered and heated with concentrated H_2SO_4 to give soluble sulphates of iron and titanium :

[1] *Z. anorg. Chem.*, 1903, 37, 18.

the mass is extracted with water, and on heating the reduced solution to boiling titanic acid is precipitated. The acid is dried and calcined at a high temperature. In practice barium sulphate is mixed with the solution before precipitation, and the small amount of calcium phosphate and barium carbonate is added to the pulp before calcination. This addition has been found to produce a more uniform product. The composite product, titanium white, is "extra" and "standard"; the latter contains 75 per cent. $BaSO_4$ and 25 per cent. TiO_2. The pigment is non-toxic and unaffected by sulphuric acid and sulphuretted hydrogen. The paints show no tendency to crack and peel, and a combination of titanium white and zinc oxide is durable. The pigment possesses greater opacity and spreading power than any other white pigment.[1]

Analysis. Volumetric Determination of Titanium Dioxide.—Russell[2] has pointed out that titanous sulphate in $4N$ sulphuric acid solution is not readily oxidised by contact with air in the ordinary course of an analysis and the necessity for titration in an atmosphere of carbon dioxide does not arise. This fact, coupled with the use of liquid zinc amalgam, renders the volumetric determination of titanium a comparatively simple and accurate process. According to Nakazono,[3] the zinc amalgam is best made by adding sufficient pure zinc to mercury to make a 3 per cent. amalgam and warming for one hour on the steam bath with dilute sulphuric acid. The product is then washed and the liquid amalgam is run off from any solid or semi-solid amalgam.

To determine the titanium by this method 1 g. of the pigment is heated in a Pyrex beaker with 25 c.c. of concentrated sulphuric acid, gently swirling to avoid caking. (U.S. specification: 20 c.c. concentrated sulphuric acid and 7 to 8 g. of ammonium sulphate.) After cooling and diluting, the liquid is filtered into a 200 c.c. flask and made up to bulk. Fifty c.c. of this solution is transferred to a separating funnel, 200 g. of the 3 per cent. zinc amalgam added and the liquid is shaken for about one minute. (U.S. specification, a Jones reductor (p. 75) is used.) The amalgam is run off as cleanly as possible and the liquid in the funnel is titrated with $N/20$ $KMnO_4$, or with standard ferric iron solution using potassium thiocyanate as indicator. The solution may be reduced and titrated again to afford confirmation. 1 c.c. $N/20$ $KMnO_4$ $=0{\cdot}00400$ g. TiO_2. The amalgam may be used for many reductions before losing its efficiency. The U.S. Government specification for titanium pigment, dry and paste, differs slightly in detail from the above, as indicated in the additions in brackets.[4] The barium sulphate may be determined by igniting and weighing the precipitate of $BaSO_4$

[1] N. Heaton, *J. Roy. Soc. Arts*, 1922; and R. H. Monk and C. Whittemore, *Canad. Chem. Met.*, 1925, **9**, 153.

[2] *J. Chem. Soc.*, 1926, **129**, 497.

[3] *J. Chem. Soc., Japan*, 1921, **42**, 526.

[4] *Circ. Bureau of Standards*, 1924, No. 163.

obtained in separating the titanium. In the U.S. specification the iron oxide is determined as follows: Prepare a standard ferric solution containing 0·0001 g. Fe per c.c. Weigh a 1 g. portion of the sample and dissolve as above, transfer without filtering to a 200 c.c. flask, cool, fill to the mark, and determine iron colorimetrically in 50 c.c. aliquot parts by ammonium or potassium thiocyanate. It is advisable to add a drop or two of $N/10$ $KMnO_4$ solution until a faint pink colour is obtained, to oxidise any ferrous iron.

III. Grey Pigments.

(Slate Grey; Stone Grey; Silver Grey; Mineral Grey.)

Slate grey is obtained by grinding and levigating special kinds of grey slate which occur in several parts of Germany, chiefly in the Eifel and near the Rhine. It is a fine yellowish- or reddish-grey powder which dries very hard as an oil colour, and is consequently used for priming paint and for the preparation of putty. It is frequently imitated by a mixture of white clay, black, ochres and ultramarine.

Zinc Sulphide Grey, *Zinc Blende*, *Calamine White*. Powdered dense zinc blende has been sold for a considerable time under these names for industrial oil painting, especially of iron bridges, etc. It is also artificially made up by tinting lithopone, etc., with charcoal black, ultramarine, and ochres, in order to obtain the light yellowish-grey tint of natural zinc sulphide grey. The latter can easily be distinguished from such preparations, for on treatment with hot hydrochloric acid it does not at first noticeably change its tint, whereas the tint of the artificial products changes owing to the decomposition of the ultramarine. On further heating, the natural product dissolves completely or leaves a slight residue of silica, and hydrogen sulphide is vigorously evolved; with the substitutes, however, barium sulphate mixed with carbon remains behind.

Zinc Grey.

This name was originally used for the *Zinc Dust* obtained on smelting zinc ores, and containing about 98 per cent. of metallic zinc. It dries hard in oil and is therefore particularly adapted for use as a paint on iron; it also preserves the iron from rust. Substitutes for this comparatively expensive colour are prepared from grey zinc oxides, which owe their colour to the presence of carbon, and are waste products in the manufacture of zinc white. They come into the market under such names as *Diamond grey*, *Silver grey*, *Platinum grey*, and they are also prepared artificially as mentioned in the preceding paragraph. They are distinguished from genuine zinc grey by the difference in specific gravity; also by estimating the zinc content, or by proving the presence of a residue insoluble in acids.

IV. Yellow Pigments.

The Yellow Ochres.

(Ochre; Yellow Earth; Oxide Yellow; Chinese Yellow.)

The typical natural varieties of ochre are disintegration products of ferruginous minerals containing felspar. The latter is broken down into clay in process of weathering. The ochres therefore represent clays coloured by ferric oxides, and their hue depends on the amount of ferric hydroxides contained, and to a lesser extent upon the degree of hydration of these hydroxides. The typical ochres must be distinguished from the siennas. The former, owing to their content of clay, possess more or less body; the latter, on account of the low content or absence of clay and the high water-content of the colouring principle, are glazing colours, and it is accordingly incorrect to include them with the ochres. The siennas also contain slight amounts of oxides of manganese. The covering power of the natural and artificial ochres (see Mars yellow) depends on the degree of hydration of the ferric oxide present. The colour of the ochres varies, according to the content of clay and the degree of hydration of the ferric oxide, from palest yellow through golden yellow to brown-yellow.

The preparation of ochres for use as paints, artists' colours, etc., is confined to the processes of crushing, levigating, sieving, drying, grinding, etc. Only the finest qualities are employed for artists' use. Standards of purity employed for artificial mineral ground-colours cannot be used in valuing ochres, for, apart from the exceptions mentioned, they are varying mixtures of the colouring components and the substratum. The chemical analysis is therefore confined to the identification of the components of the mixture, and only in special cases is a determination of the quantitative composition of value.

All ochres, especially those for use as paints, do not come into the market in the natural condition. The more brownish varieties in particular are rendered lighter in colour by the addition of white substrata, such as heavy spar, whiting, blanc fixe, and lithopone, and more brilliant by the addition of chrome yellow.[1]

The following are typical analyses of ochres from various sources:—

	Oxford Ochre.	Irish Crude Ochre.	Derbyshire Crude Ochre.	French Prepared Ochre.	American Ochre (Eastern State).
H_2O (hygroscopic).	6·89	9·05	5·40	1·80	1·30
H_2O (combined) .	8·15	12·00	6·00	9·20	3·70
CaO	1·00	0·26	0·56	0·19	...
SO_3	1·32	2·68	1·74	...	...
Al_2O_3	6·47	16·77	1·04	13·75	4·06
Fe_2O_3	12·81	26·38	76·08	20·73	11·03
SiO_2	63·48	32·50	4·39	54·00	4·47
$BaSO_4$	...	...	...	...	75·39

[1] *Cf.* Zerr and Rübencamp, *Colour Manufacture*, p. 385.

Analysis. Ochres dissolve partially in hydrochloric acid, leaving an insoluble residue of silica. Any barytes present will be found in this residue by the flame test. The solution (which should be yellow) is tested for iron, aluminium, calcium, magnesium, etc., in the usual way. Should the solution be greenish, chrome yellow is probably present, and can be detected by cooling, when crystals of lead chloride will separate, and by the usual tests for chromium. The presence of whiting is shown by effervescence with acid and the presence of calcium in the solution.

Methods for Routine Analysis of Yellow, Orange, Red, and Brown Pigments containing Iron and Manganese.

Specific Gravity. The specific gravity is determined by Thompson's[1] method, or by means of a 500 c.c. pyknometer, using c.p. benzine and 10 to 20 g. of pigment (*cf.* Vol. I., pp. 128-29).

Tinting Strength. The colours should always be compared with a carefully selected standard. 0·02 to 0·05 g. of colour is weighed out accurately, and placed on a large glass plate, and 12 drops of bleached linseed oil added; then the whole is rubbed up with a flat-bottomed pestle or muller and 1 g. of pure ZnO added. The sample is then ground with a circular motion fifty times, and gathered up with a sharp-edged spatula, ground out twice more in a like manner, giving the pestle a uniform pressure. A similar amount of the standard is next weighed out and treated in exactly the same manner. Portions of each paste are placed on a microscope slide quite close together, and a palette knife drawn across both samples so as to make them meet in a line (differences in tint are then easily seen). The tints, as shown on both sides of the glass, are compared. The amount of pigment used will vary with the tinting strength; but usually it suffices to take about 0·02 g. of the reds and about 0·05 g. of the ochres.

If it is desired to express the tinting strength of the pigment quantitatively, the standard pigment is considered to have a tinting strength of 100, and the amount of the standard pigment is varied until the tints are matched.

Added Colouring Matter. The pigment is tested successively with hot water, 95 per cent. ethyl alcohol, alcoholic soda or potash, and acetic acid, chloroform, aqueous sodium hydroxide, sulphuric acid, hydrochloric acid, stannous chloride, and other reagents may be tried. The presence of an organic colour may often be noted by the characteristic odour given off on ignition.

Analysis of Ochres.[2] The loss at 100°, loss on ignition, insoluble

[1] *Proc. Amer. Soc. Test. Mats.*, 1913, 13, 407.
[2] *A.S.T.M. Standards*, 1918, p. 660.

matter, total or soluble iron, alumina, lime, and sulphur is determined as outlined under the methods of analysis of Indian Reds, etc. (p. 494), using 1 g., or an aliquot corresponding to this weight.

Tinting strengths are tested as above. Tests should also be made for solubility in water, and reaction to litmus paper.

Lead Chromate. If lead is present, it is removed in the above scheme by nearly neutralising the filtrate from the insoluble matter with ammonia, cooling and passing in sulphuretted hydrogen to precipitate lead sulphide, which is then filtered and washed with sulphuretted hydrogen water. The lead sulphide is dissolved in hot dilute nitric acid, 10 c.c. of concentrated sulphuric acid is added, and the liquid evaporated till fumes of SO_3 are evolved. After cooling, it is diluted to 200 c.c. and allowed to stand for a few hours, then filtered on a Gooch crucible, washed with 1 per cent. sulphuric acid, ignited, and the lead sulphate weighed. The result is calculated to Pb or PbO. The filtrate from the lead sulphide is heated to expel hydrogen sulphide, oxidised with a little nitric acid and made up to volume (if working on more than 1 g.). The iron is best determined in an aliquot part by the bichromate method. Another aliquot part is treated with ammonia, the precipitate containing Al_2O_3, Fe_2O_3, Cr_2O_3, TiO_2 and phosphates.

Lime and magnesia may be determined in the filtrate.

The ammonia precipitate is dissolved in hot dilute hydrochloric acid, the paper washed with hot water, the solution cooled, oxidised with sodium peroxide, boiled to expel hydrogen peroxide, and again cooled. The cover glass is washed down and the whole diluted to about 150 c.c. and acidified with sulphuric acid. A measured excess of a standard ferrous ammonium sulphate is added, then titrated back with standard potassium bichromate solution, and the percentage of chromate calculated. Alternatively, 1 g. of the pigment is moistened with water, 5 c.c. of concentrated hydrochloric acid added, and the whole boiled for a few minutes. After cooling, sodium peroxide is added in excess, and the sample again boiled to expel hydrogen peroxide, then again cooled. Finally, the cover glass is washed off and the liquid acidified with sulphuric acid and the chromate titrated as above.

Siennas.

(Terra de Siena; Italian Earth; Mahogany Brown; Cashew Lake.)

All these earths are distinguished from the typical ochres by their high content of iron and of water, by the absence or marked decrease in the relative amount of clay, and by the presence of small amounts of oxides of manganese. They also differ outwardly from the earthy and powdery ochres since they form yellow-brown to dark brown hard lumps with a conchoidal fracture.

Mahogany brown is a sienna which has been ignited, ground wet, made up in the form of pieces, and dried. Cashew lake is a similar brown on to which organic dyes are precipitated.

The siennas are chiefly used as glazing colours in artistic and decorative painting, and especially for lacquering wood. Their covering power, like that of the ochres, is improved by calcining. The stability of ochres and siennas to light and air and their miscibility is unlimited.

The darkening of ochres, and especially of unburnt sienna in oil, probably arises from their slight solubility in fatty oils, or from the gradual decrease in water-content of the hydrated ferric oxides, with production of darker coloured lower hydrates.

Analysis. Typical analyses are as follows:—

	Roman Sienna.			American Sienna.
	I.	II.	III.	
H_2O (hygroscopic)	17·55	8·25	12·40	7·0
H_2O (combined and organic matter)	9·00	11·00	9·40	6·2
SiO_2	22·66	17·41	5·02	6·76
$CaCO_3$	0·96	1·07	4·46	...
Al_2O_3	2·84	5·18	7·26	5·23
MnO_2	1·19	0·63	1·46	...
Fe_2O_3	45·82	57·03	59·96	74·81
MgO	...	...	trace	...

(Hurst and Heaton, *Painters' Colours*, etc., p. 196.)

Methods of Analysis of Siennas (and Umbers).[1] After gently roasting to destroy organic matter, a test is made as under "Analysis of Indian Reds," etc., p. 494.

Manganese may be determined *volumetrically* by the bismuthate method. One g. of the sample is ignited gently in a platinum dish to destroy organic matter, then cooled, and 10 c.c. of water, 4 c.c. of concentrated sulphuric acid, and about 20 c.c. of hydrofluoric acid (if necessary a little sulphurous acid) added. After evaporating until the sulphuric acid fumes freely, the sample is cooled and dissolved in 25 c.c. of nitric acid (1 : 3).

If no appreciable residue remains, the liquid is transferred to a 100 c.c. graduated flask, using 25 c.c. of the same dilute acid to rinse the dish, then diluted to the mark with water and mixed thoroughly. If there is an appreciable residue, it is filtered on a small filter, washed with water, the residue ignited in a platinum crucible, and fused with a little sodium or potassium pyrosulphate. It is then dissolved in water with the addition of a little nitric acid, added to the main

[1] *A.S.T.M. Standards*, 1918, p. 661.

filtrate, evaporated nearly to dryness, taken up in nitric acid (1 : 3) and transferred to the flask as before. An aliquot of 10-15 c.c. is pipetted into a 200 c.c. Erlenmeyer flask, and 30 c.c. of water and 10 c.c. of concentrated nitric acid (sp. gr. 1·4) and about 0·5 g. of sodium bismuthate added. After heating for a few minutes or until the pink colour has disappeared (with or without the precipitation of manganese dioxide), a few small crystals of sodium or potassium nitrite are added to dissolve the dioxide and the solution is boiled for several minutes to expel the nitrous fumes, a little sodium carbonate being added. Water is added to bring the volume up to 50 c.c., the liquid cooled to about 15°, then about 0·5 g. of bismuthate added and the whole well shaken. Fifty c.c. of water containing 30 c.c. of nitric acid to the litre is added and the whole filtered by suction through an asbestos felt into a 300 c.c. Erlenmeyer flask. The filter is then washed with 50-100 c.c. of the same acid and a measured volume of standard ferrous ammonium sulphate solution is run in. Finally, the liquid is titrated back to a faint pink colour with standard permanganate. The number of cubic centimetres of the permanganate solution obtained, subtracted from the number corresponding to the volume of ferrous solution used, will give the volume of permanganate equivalent to the manganese in the sample, which, multiplied by the value of the $KMnO_4$ in Mn, gives the weight of manganese in the portion used.[1]

Manganese may be determined gravimetrically after the preliminary separation of iron and aluminium by precipitation as hydroxides by means of pyridine, according to the method of Moore and Meller.[2] Manganese remains unaffected.

One g. of the pigment is treated in a 200 c.c. covered beaker with 20 c.c. of concentrated hydrochloric acid, gently boiling until the pigment is decomposed. Distilled water is added and the liquid is again brought to the boil. The insoluble matter is allowed to settle and the supernatant liquid is filtered. The residue is treated afresh with 10 c.c. of acid, diluted as before and filtered. The combined filtrates (about 200 c.c.) from the insoluble matter are rendered as nearly neutral as possible, using ammonia, and the iron and aluminium hydroxides are precipitated with pyridine, using a slight excess only. The precipitate is coagulated by digesting for five minutes on a water bath, filtered through an ashless paper and washed with water containing a few drops of pyridine. At this concentration manganese is not carried down, even if completely oxidised and only one precipitation of the iron and aluminium is necessary. The filtrate is slightly acidified with hydrochloric acid, hydrogen peroxide added, and the manganese is precipitated with ammonia, filtered, washed, strongly

[1] Lord and Demorest, *Metallurgical Analysis*, 1913, p. 82.

[2] *J. Amer. Chem. Soc.*, 1908, **30**, 593.

ignited and weighed as Mn_3O_4. Alternatively, the precipitate may be dissolved in dilute sulphuric acid, a sufficient quantity of oxalic acid solution added and the excess titrated with standard permanganate solution.

The Examination of Mineral Colours for Arsenic.

Methods for the approximate estimation of small quantities of arsenic are fully described in Vol. I., pp. 433-448.

C. Fischer,[1] in examining mineral colours for arsenic, made use of the method of Mayrhofer, in which arseniuretted hydrogen is evolved and led into an *N*/100 silver nitrate solution, and the excess of silver titrated back with *N*/100 thiocyanate solution. Out of 27 commercial samples examined, 13 gave no arsenic mirror in Marsh's apparatus, 10 gave a faint, transparent mirror indicating under 0·01 per cent. As_2O_3, and 4 gave a strong opaque mirror.

Gutzeit Test. A 4-oz. bottle is fitted with a rubber stopper carrying a glass tube about 10 inches long, the end of which projects about ¼ inch through the bottom of the stopper. The tube carries two plugs of cotton-wool at the lower end, and a roll of lead acetate paper occupying nearly the whole length of the tube. Over the upper end of the tube a cap of filter paper, previously soaked in mercuric chloride solution and dried, is fastened by means of a rubber band. One g. or a suitable quantity of the pigment is placed in the bottle, 10 g. of arsenic free zinc added, followed by 10 c.c. of arsenic free hydrochloric acid containing 1 c.c. of stannous chloride solution (see below) per 100 c.c. of the acid. The stopper is replaced and the action allowed to proceed for forty minutes. The yellow stain which develops on the prepared filter paper is compared with those obtained from standard arsenic solutions. This process, which detects one part of arsenious oxide in 2 millions, is more suitable for pigments than Marsh's test or its electrolytic modification.

The stannous chloride solution is prepared as follows: Ten g. of tin is treated with 30 c.c. of concentrated hydrochloric acid and 10 c.c. of distilled water, warming on a steam bath to aid complete dissolution, and the bulk is made up to 50 c.c. with distilled water. A further 50 c.c. of concentrated hydrochloric acid is added and the solution is boiled down to 50 c.c., filtered and tested for arsenic. If present, a further 50 c.c. of acid is added and the boiling repeated.

It is important to watch the zinc used in the process, since pockets containing arsenic are occasionally found in supplies which are for the most part free.

[1] *Chem. Zentr.*, 1903, I., 995.

Artificial Ochres.

(Mars Yellow; Siderin Yellow.)

These yellow iron colours are prepared, according to one method, by dissolving ferrous sulphate in water so as to obtain a solution of sp. gr. 1·06, warming in earthenware vessels, and introducing strips of sheet zinc. The precipitate which separates out forms, after being washed and dried, a bright yellow ochre-coloured and extraordinarily delicate powder similar in tone to dark Naples yellow. Darker rust-yellow varieties are said to be obtained by using ferric chloride in place of ferrous sulphate. According to another process a solution containing equal parts of ferrous sulphate and alum is treated with sodium carbonate, the mixed aluminium and iron precipitate is thoroughly washed, and dried at a moderate temperature. This colour is known as *Mars yellow*. By slight calcination it is converted into *Mars orange*; by calcining at a red heat into *Mars purple*, and by calcining at a white heat into *Mars violet*. These colours are dearer than the natural ochres, and they are used almost solely as artists' colours. They should not contain any basic sulphates. A bright orange-yellow colour which is a basic ferric chromate is sold under the name of *Siderin yellow*. It is described by Mierzinski as particularly applicable for water-glass painting. It is, however, little used. Nothing disadvantageous is known as regards the permanency in light and compatibility of these pigments. Mars colours can be distinguished from the ochres and ochre reds by being soluble in concentrated HCl and by containing a large proportion of alumina, but no silica.

Realgar (As_2S_2).

Orpiment (As_2S_3).

(King's Yellow.)

These naturally occurring sulphides of arsenic are also obtained as by-products in the roasting of arsenical pyrites. They are characterised by their poisonous properties, sensitiveness to light, and incompatibility with certain other colours, and are easily recognised by their volatility on being heated alone, and by the arsenical odour evolved when heated on charcoal. They form colourless solutions with strong hydrochloric acid, also with caustic soda, from which, on adding acid, the pigment is reprecipitated.

Naples Yellow.

(Antimony Yellow; Paris Yellow.)

Naples yellow is essentially basic lead pyro-antimonate with varying quantities of lead oxide or free antimonic acid. Neutral lead antimonate is white and becomes yellow when heated, owing to conversion into the pyro-antimonate.

Two varieties are prepared, viz., light and dark. The colour of light Naples yellow, if arising from excess of lead oxide, can be improved by treatment with dilute nitric acid. The tone of Naples yellow depends not only on the proportions in which the components are mixed, but also inversely on the temperature employed. The pigment, therefore, does not possess a constant percentage composition. The lighter varieties prepared with zinc oxide, etc., and whose chief coloured component is lead pyro-antimonate together with lead oxide, are applicable as substrata. Besides lead and antimony all genuine Naples yellows contain varying quantities of chlorine present as basic lead chloride (Mineral yellow, Turner's patent yellow, Cassel yellow), which is not, therefore, an addition or adulteration. It results, rather, from the reaction of the flux—viz. common salt—with the lead compound which serves for the preparation of the colour.

A considerable amount of imitation Naples yellow which is on the market is prepared by mixing cadmium sulphide with zinc oxide, barytes, etc.

Analysis. For the purpose of identifying and estimating the chief components, Naples yellow is fused with sodium carbonate and sulphur, and the melt extracted with water. The black residue contains the lead as sulphide and the zinc, if present. The yellow solution consists of sodium thio-antimonate, possibly mixed with sodium thio-stannate. The lead, zinc, and antimony are separated and estimated by the ordinary analytical methods.

In rare cases adulteration of Naples yellow with chrome yellow or chrome orange occurs. On warming the colour with hydrochloric acid a green solution is obtained in this case.

The shade of genuine Naples yellow has been imitated by mixing orange-coloured cadmium yellow with zinc white, or more rarely with white lead. The use of this mixture as an artists' colour, and especially as a water colour, is inadvisable on account of the properties of zinc white (p. 452).

A pigment related to Naples yellow was formerly made under the name of *Antimony yellow*, which was a mixture of oxychlorides of bismuth and lead with lead antimonate.

Genuine Naples yellow is a strong body colour, completely stable as regards weather conditions, and therefore applicable as a lime colour. It has the disadvantage of being somewhat gritty and does not work well. It is also stable on ignition, and is therefore used for painting on glass and porcelain. On the other hand, like all lead pigments it is affected by hydrogen sulphide, but the coloration disappears again on exposure to light, or on treatment with hydrogen peroxide. On account of its relatively high price Naples yellow

is chiefly used as an artists' colour, but its use is now nearly obsolete.

It is quite fast to light, but mixtures of Naples yellow with zinc yellow, baryta yellow, or zinc green gradually darken.

Turner's Yellow.

(Mineral Yellow; Veronese Yellow; Cassel Yellow; Kassler Yellow.)

Turner's yellow is a basic lead chloride of varying composition, frequently corresponding to the formula $PbCl_2 + 7PbO$. For its preparation 10 parts of red lead and 1 part of sal-ammoniac are heated to fusion; metallic lead separates out at the bottom of the crucible, while the yellow oxychloride forms above. A Cassel yellow containing alumina, and used as an enamel, is prepared by heating together equal parts of white lead, sal-ammoniac, and alum in a crucible. This pigment has become obsolete since the introduction of the chromes.

The proportion of lead chloride to lead oxide, a frequently varying figure, is determined by dissolving the colour in dilute nitric acid and a large quantity of warm water, care being taken to prevent evolution of chlorine. Silver nitrate is then added to the solution, and from the weight of silver chloride obtained the amount of lead chloride present may be calculated.

Tungsten Yellow.

This consists of tungstic acid and is prepared by decomposing wolframite with sodium carbonate, acting on the alkali tungstate with calcium chloride, adding the resulting calcium tungstate to warm hydrochloric or nitric acid, and washing the precipitated tungstic acid. Tungsten yellow is either fiery lemon-yellow in colour with a greenish cast, or orange-yellow, according to the manner in which it is purified. It becomes faintly green on exposure to light, a change said to be due to the alkali it contains.[1]

Litharge and Massicot.

Yellow oxide of lead is now seldom used as an independent colour, and, as massicot, serves principally as the raw material for the preparation of red lead.

Litharge is obtained as a by-product in the process of smelting silver, and differs from *Massicot* by its decided reddish colour. According to Zerr and Rübencamp, it is to be looked upon as fused and crystalline lead oxide which must first be converted into the pulverulent commercial form by grinding. Litharge is unsuitable for the preparation of red lead, as it can only be further oxidised with difficulty.

[1] Mierzinski, *Handb. der Farbenfabrikation*, 1898, vol. i., p. 426.

The preparation of massicot is carried out in specially constructed reverberatory furnaces in which oxidation of the lead can take place without fusion of the oxide, and in which it is obtained in the finest possible state of division, when it is more readily oxidised to red lead. (*Cf.* Red Lead, p. 498.) The preparation from white lead is now no longer usual.

The analysis of litharge is described in the section on "Non-Ferrous Metals," p. 240.

Uranium Yellow.

This pigment is prepared by roasting pitchblende with sodium carbonate and potassium nitrate, whereby soluble uranyl sodium carbonate is obtained, which, after removal of impurities by addition of sodium carbonate, is neutralised with sulphuric acid, when uranium yellow is precipitated in the form of a delicate light yellow powder. It is a hydrated sodium uranate with the formula $Na_2U_2O_7+6H_2O$.

On addition of caustic soda to the solution of the uranyl sodium carbonate obtained as described above, a precipitate of darker colour is produced known as *Orange-coloured Uranium yellow*. On ignition it passes into anhydrous *Dark Orange-coloured Uranium yellow*. The uranium colours are chiefly used for porcelain painting and for the preparation of uranium glass, which is characterised by its green fluorescence.

Cadmium Yellow and Cadmium Orange.

(Jaune de Cadmium ; Cadmium gelb ; Jaune Brillant.)

Cadmium yellows are sold in different shades under the designations lemon, pale, medium, dark and orange, or as Nos. 0-6 and 1-7 respectively, the lowest figure denoting the palest tone. As regards the preparation and chemical composition of the commercial varieties of cadmium yellow, there are few definite statements even in the latest literature. They are obtained in the wet way either by passing hydrogen sulphide into solutions of cadmium salts or by precipitating with alkali sulphides, and also in the dry way by strongly heating cadmium carbonate with sulphur ; and to some extent the various shades obtained by these different methods are under the control of the manufacturer

A. Sauvageot[1] states that the only practical process which yields a product free from sulphur and of bright colour and pure tone is the interaction of an insoluble cadmium salt with a soluble alkaline sulphide. The paler shades are made from cadmium oxalate and the deeper shades from cadmium carbonate, the temperature influencing the exact shade obtained.

The problems connected with the manufacture of cadmium yellow have been reviewed by H. Heppler and by Freitag.[2]

[1] *Rev. Prod. Chim.*, 1925, **28**, 397. [2] *Farbe u. Lack*, 1926, No. 16, 196, and 1925, No. 48, 568.

It is frequently maintained that all varieties of cadmium yellow prepared in the wet way are pure cadmium sulphide (CdS). Follenius[1] found, that on passing hydrogen sulphide into solutions of cadmium salts chemically pure cadmium sulphide could not be obtained, as it always contained up to 2 per cent. of the cadmium salt from which it was precipitated. These technical accessory components of cadmium sulphide cannot be removed by washing, and (like the red lead sulphochloride, etc.) they are either present as double salts or else are adsorption mixtures with the cadmium sulphide. On ignition this impurity volatilises as a simple cadmium salt leaving pure cadmium sulphide behind.

The shades of technically pure, unadulterated cadmium sulphides depend on the manner of preparation. All cadmium sulphides prepared in the dry way and those prepared in the wet way and subsequently ignited have approximately the same shade, a very pale golden yellow with a dull ochre-yellow tint; the purple-red discoloration which appears on ignition disappears on cooling. Their hue is not identical with that of the lightest varieties prepared in the wet way, *e.g.* "Cadmium lemon" or Nos. 0-1. When the preparation is carried out by treating solutions of cadmium salts with alkali sulphides, only a dull orange-yellow sulphide is usually obtained. The orange-coloured precipitate (probably oxysulphide) often obtained at first, rapidly changes on standing into light golden yellow, which becomes orange on drying. The pigment so obtained is not cadmium sulphide (CdS) but probably the hydroxy-hydrosulphide Cd(SH)(OH).[2] This variety of cadmium yellow easily passes into colloidal solution. The precipitates obtained by treating either hot or cold solutions of cadmium salts with hydrogen sulphide in presence of excess of acid deepen in colour from palest whitish-yellow and lemon at first up to deep orange-yellow. The change depends on concentration, temperature, and the amount of acid in the solutions, and takes place both during the passing in of the hydrogen sulphide and on washing. The only stable tones obtained, after drying the precipitate, are a deep golden yellow and a pale orange-yellow respectively. The palest lemon and golden yellow cannot be obtained in the dry state by this method.

The causes of the colour-change of cadmium sulphide precipitated by hydrogen sulphide have been investigated by A. H. Church (1876), G. Buchner, who found that only two modifications are formed in the wet way, a lemon-yellow α modification, sp. gr. 3.9, and a β vermilion variety, sp. gr. 4.5. Both modifications are chemically identical, and the α modification can be changed by rubbing into the β form;[3] and also by

[1] *Z. anal. Chem.*, 1874, **13**, 411.
[2] A. Eibner, *Farben-Zeit.*, 1908, **13**, 1511, 1549.
[3] *Chem. Zeit.*, 1887, **11**, 1087, 1107.

A. W. Keim, N. von Klobukow,[1] K. Haushofer[2] and T. Niederländer.[3] It was found that the specific gravity of the paler varieties of cadmium yellow was 3·9-4·5, and that of the dark varieties 4·5-4·8, a variation similar to that observed in the case of natural cadmium sulphide, Greenockite (4·5-5·9). Further, it was shown by Haushofer that all artificially prepared cadmium yellows are crystalline, and, with one exception (monoclinic), belong to the hexagonal system. The observations made by W. Ostwald on precipitated and crystallised mercuric oxide render it, however, very probable that the variations in colour are due to varying size of grain.

The product obtained by precipitation from solutions is superior in covering power and in colour to that obtained by heating together cadmium oxide with excess of sulphur. The precipitate is bright citron yellow from weakly acid and orange yellow from strongly acid solutions. After being washed they should be dried at a temperature not exceeding 86°.[4]

Cadmium colours and their suggested application to the paint industry have been discussed by H. W. Dudley Ward,[5] who describes cadmium zinc mixtures of a pale lemon shade, cadmium lithopone (cadmopone) and cadmium sulphoselenides of orange to full vermilion red shades (cadmium red, selenium red and fire red).

The most frequent adulterants of commercial cadmium yellow are: arsenic yellows, barytes, chrome yellows, clay, gypsum, tin sulphide, zinc carbonate, zinc chrome, zinc oxide and zinc sulphide.

Qualitative Analysis. For the purpose of testing varieties containing cadmium oxalate or carbonate qualitatively, A. Eibner heats a portion in a glass tube. If a strong bright metallic mirror quickly appears, then cadmium oxalate is present, which, on decomposition, gives metallic cadmium. Preparations containing cadmium carbonate give a faint mirror only after long heating. Carbon dioxide is identified by warming a portion of the substance with dilute sulphuric acid. Zinc is recognised by extracting with warm acetic acid and testing the filtrate with ammonium sulphide.

According to G. Buchner,[6] technically pure cadmium yellow should react as follows: (1) It should dissolve on warming with dilute hydrochloric acid to a clear and colourless solution (absence of free sulphur, heavy spar, and chrome yellow). (2) It should not contain any components soluble in water. (3) After agitation with acetic acid it should give a filtrate in which no cloudiness or precipitate is produced by potassium hydroxide (absence of any considerable quantities of

[1] *J. prakt. Chem.*, 1887, **39**, 412.
[2] *Ibid.*
[3] *Techn. Mitt. f. Malerei*, 1893, **10**, 424, and *J. Inst. Met.*, 1919, **1**, 463.
[4] N. F. Budgen, *Chem. Trade. J.*, 1924, 641.
[5] *J. Oil and Col. Chem. Assoc.*, 1927, **10**, 4.
[6] *Chem. Zeit.*, 1887, **11**, 1087, 1107, and *Moniteur de la Science*, 1888, vol. ii.

zinc compounds or cadmium salts [substrata]). (4) Heated in a tube or on platinum foil it should become purple-red, and on cooling pure yellow again, but not brownish-yellow (absence of cadmium hydroxy-hydrosulphide or carbonate). (5) After agitation with ammonium hydroxide it should give a filtrate which is not coloured yellow by hydrochloric acid (absence of arsenic compounds). (6) Heated in a tube it should not give off any considerable amount of water, or ammonia instead of sulphur dioxide, and according to Eibner should not produce a metallic mirror (absence of cadmium and zinc hydroxy-hydrosulphides, and cadmium oxalate and carbonate as substrata). Technically pure cadmium yellow prepared in the wet way gives off only traces of water and sulphur dioxide when heated in a tube. A thin white deposit always forms above the substance, and is due to the sublimation of the cadmium salts (chloride, sulphate), which are carried down with the sulphide precipitate and cannot be removed by washing.

Quantitative Analysis: (a) *Technically Pure Commercial Varieties.* If the qualitative analysis shows that the sample is not a cadmium substratum pigment, then the substance is dissolved in hydrochloric acid, the cadmium precipitated by hydrogen sulphide and estimated as sulphide, after igniting with sulphur in a current of hydrogen; or the cadmium sulphide is converted into sulphate and weighed as such. By sublimation, or by boiling the colour with sodium carbonate solution, the cadmium chloride or sulphate present can be determined by difference.

(b) *Substratum and Adulterated Varieties of Cadmium Yellow.* The analytical procedure is determined by the results of the preliminary qualitative examination. Estimations of the following substances are also involved: water, carbon dioxide, oxalic acid, sulphur, ammonia, and hydrated oxides of zinc and cadmium. The latter are extracted with dilute acetic acid, and estimated as described above. Cadmium yellow is very seldom adulterated with heavy spar, chrome yellow, etc.

Properties. The technically pure varieties of cadmium yellow (medium, dark, and orange) are pronounced body colours. On the other hand, the palest varieties, since they contain substrata of only low refractivity, are much inferior in covering power. Cadmium hydroxy-hydrosulphide, in contrast to anhydrous cadmium yellow, is a pronounced glazing colour. In addition to these an orange-yellow hydroxy-sulphide, $Cd_2S(OH)_2$, has been prepared by Buchner.

Fastness to Light. Only those commercial varieties of cadmium yellow which consist of technically pure cadmium sulphide are fast to light when in the form of powder and in water-colour washes, so far as experiments with this comparatively new pigment have demonstrated up to the present. On the other hand, all cadmium substratum colours

in powder form and in water-colour washes are fugitive in light; the most fugitive are those rich in zinc. In powder form they fade (formation of white basic sulphates), while in water-colour washes a change of colour to greenish-brown appears first of all; later they become bleached. The causes of this colour change are unexplained. In addition, cadmium hydroxy-sulphide (Buchner), glazing cadmium yellow, cadmium hydroxy-hydrosulphide (Eibner), and the substances prepared by precipitation with alkali sulphide and containing sulphur, are fugitive in light. Modern manufacturers in this country are now able to produce bright light yellow cadmium sulphide of reasonable purity. The middle and deep shades of cadmium yellow are permanent.

Behaviour in Mixtures. Cadmium yellow can be mixed with almost all other pigments without affecting them or being affected by them, the only exceptions being those pigments which contain lead or copper as their basis, *e.g.*, white lead, emerald green, and the chrome yellows.

Cadmium lithopone in which the zinc of standard commercial lithopone is replaced by cadmium shows good covering properties and a high tinting strength—an admixture of 5 per cent. of cadmium lithopone with 95 per cent. standard lithopone gives a cream yellow—when rubbed out in oil.

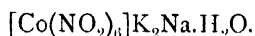
Jaune brillant is an admixture of cadmium yellow and white lead; this colour is inclined to darken owing to the formation of black lead sulphide.

Cobalt Yellow (Aureolin).

This pigment is exclusively an artist's colour. It is usually prepared by rendering a solution of cobalt nitrate alkaline with caustic potash, diluting it with acetic acid, and treating it, whilst hot, with a concentrated solution of potassium nitrite. The crystalline precipitate which slowly forms is orange-yellow at first, then becomes brownish, and after being washed is light golden yellow. It is a potassium cobalti-nitrite of the composition $[Co(NO_2)_6]K_3$, with varying amounts of water. According to Church, the pigment usually contains 3 mol., and under other conditions 4 mol. of water,[1] when it has a greenish tint. Church states that the anhydrous form is obtained by treating a solution of a cobalt salt acidified with acetic acid, with a concentrated solution of potassium nitrite, and keeping the mixture warm. The pigment is said to be obtained in an even more beautiful form when a current of nitric oxide mixed with air is passed into a solution of cobalt nitrate and potassium acetate, potassium carbonate being added from time to time (Rosenheim and Koppel).

[1] *Cf.* also, Rosenheim and Koppel, *Z. anorg. Chem.*, 1898, **17**, 59.

According to R. H. Adie and T. B. Wood,[1] a particularly lustrous cobalt yellow is prepared by adding a solution of sodium cobalti-nitrite, acidified with acetic acid, to a dilute solution of potassium acetate or nitrate. The pigment obtained in this way possesses the composition :—

$$[Co(NO_2)_6]K_2Na.H_2O.$$

Church states that it is equal in value to the other varieties of aureolin. As a water colour it has the advantage of being much less soluble in water than the older pigments of this class, and of not sinking so deeply into the paper. The water can be partially driven off by heating to 115°. The slow drying of aureolins as oil colours and the dirty appearance which they assume are due, as Church has pointed out, to the presence of water.

As regards fastness to light and compatibility of these pigments in mixtures with others, divergent opinions exist. According to Mierzinski and Zerr and Rübencamp, cobalt yellow is unstable in the light. J. Bersch and Church describe it as permanent in water-colour washes. According to experiments made by Church, its intensity diminished 10 per cent. within ten years. A. Eibner's experiments proved that as a water-colour wash exposed to direct sunlight for six years it showed no change. According to Gentele, it is miscible with most other colours, even with those containing sulphur. A. W. Keim observed instability in mixtures with several other pigments. These varying opinions can probably be traced to differences in the water-content of the individual varieties.

Analysis. Cobalt yellow is perceptibly soluble in water; it is only feebly attacked by solutions of alkalis and dilute acids, and is only slowly blackened by hydrogen sulphide. Ammonium sulphide decomposes it immediately. When heated it decomposes, giving off brown fumes of nitrogen dioxide, and leaves a black residue of cobalt oxide and potassium hydroxide, which has an alkaline reaction and dissolves in dilute acids forming a red solution.

The name *Jaune Indien* or *Indian yellow* which is sometimes given to cobalt yellow is a false "substance designation" intended to suggest its similarity with genuine Indian yellow (Puree). This similarity, however, does not exist either as regards colour tone, genuine Indian yellow having a brownish tint, or in properties of technical importance in painting, since Indian yellow is a glazing colour, and cobalt yellow a body colour.

[1] *J. Chem. Soc.*, 1900, 27, 1076.

Nickel Yellow.

This pigment is obtained by treating nickel sulphate with sodium phosphate and calcining the resulting precipitate. According to Mierzinski and Zerr and Rübencamp, the colour is very stable and of good covering power.

The Yellow Chromium Pigments.

Chrome Yellow.

(a) *Technically pure Varieties of Chrome Yellow.* These are, essentially, neutral lead chromate, and vary in shade from pale to dark golden yellow. According to Zerr and Rübencamp,[1] the shade of these commercial preparations depends upon the concentrations of the solutions of the reacting substances, their temperature, the way in which they are brought together, the period of reaction, and the manner in which the precipitated pigment is washed. The preparation is carried out with dilute solutions at the lowest possible temperature, and the solutions are kept in constant motion during the precipitation. The precipitation and the washing process must be carried out rapidly. K. Jablczynski[2] has pointed out that chrome yellow undergoes partial hydrolysis on washing, whereby some chrome red is formed which causes subsequent darkening. It is stated that this phenomenon does not occur if the washing process is not exhaustive, or if an excess of at least 5 per cent. of lead acetate is used in the precipitation.[3] According to Gnehm, this darkening does not take place when lead nitrate is used instead of lead acetate, provided that a slight excess is employed.

(b) *Chrome Yellow Substratum Colours.* The lemon-yellow shade of chrome yellow, for which there has been a demand since the introduction of zinc yellow, cannot be obtained by observing the above precautions, as they do not prevent the increase of density of chrome yellow owing to increase in size of grain.[4] Double salts of lead chromate and lead sulphate (lead sulpho-chromates possessing the composition $PbCrO_4 . PbSO_4$ and $PbCrO_4 . 2PbSO_4$), varying in tint from sulphur-yellow to lemon-yellow, have been known for a considerable time.[5] The commercial brands of "lemon" chrome yellow are therefore prepared in such a way that, simultaneously with the precipitation of chrome yellow from very dilute solutions, a definite amount of lead sulphate in a very finely divided condition is produced, which is taken up by the chrome yellow, forming the double salts.

[1] *Colour Manufacture*, p. 130.

[2] *Chem. Ind.*, 1908, **31**, 731; *J. Soc. Chem. Ind.*, 1909, **28**, 30; *Farben-Zeit.*, 1909, **14**, 1041.

[3] According to Zerr and Rübencamp, 37½ parts of bichromate to 100 parts of lead acetate.

[4] *Cf.* H. Amsel, *Z. angew. Chem.*, 1896, **9**, 613.

[5] M. Willenz, *Bull. Assoc. Belg. des Chim.*, 1898, **12**, 163; *Fischer's Jahresber. f. Chem.*, 1898, p. 417.

This prevents the production of more complex and more deeply coloured products.[1] Jablczynski is of opinion that the durability of the lemon-yellow tone of this chrome yellow is due to the lead sulphate dissolving sufficiently in water to prevent the hydrolysis of the pigment on washing.

The influence of raw materials, impurities, concentration, temperature, degree of agitation, etc., on the precipitation and dispersion of pure lead chromate and mixtures of chromate and sulphate has been investigated by H. Wagner and E. Keidel[2] and the existence of mixed crystals in the sulphate chromes is discussed. An interesting account of some of the applications and properties of chrome pigments and the methods for stabilisation of the colour of pale chromes is given by W. J. Palmer.[3]

(c) *Adjuncts to Chrome Yellow Colours.* Since technically pure chrome yellow is too dear for various industrial purposes, adjuncts such as gypsum, heavy spar, China clay, whiting or white infusorial earth are added to it in order to reduce the cost. These inferior qualities are known as Baltimore chrome yellow, American or French chrome yellow, Imperial, King's, Canary, Cologne, Leipzig, New, Paris, Lemon, Zwickau yellow, etc.

Chrome Orange and Chrome Red (Derby Red).

These pigments consist of basic chromate of lead, $Pb_2(OH)_2CrO_4$, or of mixtures of this with neutral chrome yellow. They are prepared either by treating basic lead acetate with potassium or sodium bichromate, or by agitating lead sulpho-chromates with caustic soda in hot solution. The designations "Chrome Cinnabar," "Chrome Garnet," and "Chrome Ruby" are used for the deepest shades of chrome red.

The shades of the chrome oranges and chrome reds depend on the size of grain, as is shown by the fact that these pigments do not stand fine grinding. They lose thereby in depth and richness, and assume pale to dark orange tones.

Valuation of the Yellow and Red Chromium Colours.

Examination of Chrome Yellow.—When chrome yellow is boiled with strong hydrochloric acid a green solution containing the chlorides of chromium and of lead is obtained from which the latter separates on cooling in white crystals. Chrome yellow is dissolved by boiling with caustic soda solution, and is re-precipitated on addition of acetic acid to the solution. The complete analysis, which is seldom necessary, is

[1] Milbauer and Kohn, *Z. physikal Chem.*, 1916, **91**, 410.

[2] *Farben-Zeit.*, 1926, **31**, 1567.

[3] *J. Oil and Col. Chem. Assoc.*, 1925, **8**, 90.

carried out in the usual manner by reducing a solution of the substance with hydrochloric acid and alcohol. The solution is then cooled and treated with strong alcohol, and the lead chloride which separates out collected on a tared filter paper, previously dried at 120°. The precipitate is washed with alcohol, dried at 120°, and weighed. The chromium contained in the filtrate is precipitated as hydroxide by ammonia, too great an excess of the reagent being avoided.

The more important adulterants of chrome yellow are clay, heavy-spar, lead sulphate, gypsum, chalk, and alumina. These substances are determined qualitatively by Wittstein's method[1] as follows:—1 g. of the sample is treated in a flask with 7 g. of pure hydrochloric acid of sp. gr. 1·12; effervescence indicates the presence of chalk. The mixture is heated until the remaining sediment is quite white and permanent, 1 g. of 90 per cent. alcohol is then added, and the heating continued until the colour of the solution is pure green. One hundred c.c. of water is added, the solution filtered, and the precipitate washed until the washings no longer give reactions for free acid or sulphate. The residue on the filter paper may consist of heavy spar and clay, which can be separated by the usual methods. The filtrate is tested with barium chloride; if sulphates (lead sulphate and gypsum) are present 1 g. of sodium sulphate is added to the solution, which is stirred until the salt is dissolved, and then allowed to settle. A precipitate indicates the presence of lead sulphate; this is filtered off, the chromium and alumina in the filtrate precipitated with ammonia, and the second filtrate tested for calcium (gypsum).

C. T. Hough[2] estimates chromium in chrome yellow as follows: 0·5 g. of the sample is heated with 15 c.c. of 20 per cent. sodium hydroxide, and the solution cooled and diluted to 200 c.c. Two g. of ferrous ammonium sulphate dissolved in a little water is then added, the mixture stirred and allowed to stand for a few minutes and then acidified with dilute sulphuric acid, diluted to twice its volume, and titrated with standard permanganate. For the detection of chromium in mixed pigments Hough recommends that the sample be stirred with a few cubic centimetres of dilute nitric acid (1 : 5), filtered, and the filtrate tested with a few cubic centimetres of hydrogen peroxide. A purple coloration, due to perchromic acid, indicates chromium.

Adulteration with lead sulphate can also be easily detected by Löwe's method[3] as follows:—The finely powdered chrome yellow (or chrome red) is shaken with a cold, moderately strong solution of sodium thiosulphate, in which lead sulphate is readily soluble. Lead can be recognised in the filtrate by treating with neutral potassium chromate,

[1] *Dingl. polyt. J.*, 1873, **210**, 280.
[2] *Ind. Eng. Chem.*, 1919, **11**, 767.
[3] *Polyt. Notizbl.*, 1873, p. 369.

and estimated quantitatively by precipitation from this solution with sulphuretted hydrogen. The lead sulphide thus obtained is washed, and converted in the usual manner into lead sulphate. J. Milbauer and I. Sellik describe a method of separation of lead by electrolysis in the analysis of chrome yellows.[1]

For the estimation of heavy spar, gypsum, chalk, barium carbonate and lead sulphate, H. Amsel[2] suggests the following method:—Half a gram of the sample is shaken with 10-15 c.c. of 10 per cent. potassium hydroxide solution in a beaker, and after addition of 10 c.c. of water the mixture is boiled for five to ten minutes over the free flame. All lead compounds, together with calcium sulphate, are thus dissolved, only barium sulphate and calcium carbonate, if present, remaining insoluble. Without filtering, the alkaline solution is then strongly acidified with concentrated hydrochloric or nitric acid; the alkali plumbite is thereby converted into soluble lead chloride or lead nitrate, and any calcium carbonate present is dissolved. The solution is again boiled, and then filtered; the heavy spar remaining on the filter paper is well washed with hot water, dried, ignited, and weighed. The acid filtrate is neutralised with sodium carbonate, a little bromine water is added to ensure complete oxidation, and the solution heated on a gently boiling water-bath until it no longer smells of bromine. The insoluble carbonates are then filtered off from the solution of sodium chromate and sulphate, and the solution is acidified with hydrochloric acid, evaporated to dryness in a porcelain dish to remove completely any remaining traces of bromine, the residue dissolved in about 30 c.c. of water, a few drops of hydrochloric acid added, and finally 5 c.c. of alcohol, whereby the chromate is reduced to a chromic salt. A portion of the bromine is retained by the excess of sodium carbonate and is only set free again after acidifying; it is, therefore, absolutely necessary to evaporate to dryness before proceeding with the reduction. After reduction is complete—that is, when the liquid no longer smells of alcohol—excess of ammonia is added, and the solution warmed for ten to fifteen minutes on the water-bath; it is advisable to add more water if the solution has become too concentrated. The precipitate, which does not come down immediately, is filtered off, washed well with hot water, dried, ignited in a porcelain crucible, and weighed. From the weight of Cr_2O_3 obtained, the CrO_3 may be calculated.

The ammoniacal filtrate is acidified with hydrochloric acid, and the sulphuric acid, if present, estimated as barium sulphate in the usual manner.

The carbonates of calcium and lead, and possibly lead peroxide remaining on the filter paper, are dissolved in hydrochloric acid; lead

[1] *J. prakt. Chem.*, 1919, **99**, 85.
[2] *Z. angew. Chem.*, 1896, **9**, 613; *J. Soc. Chem. Ind.*, 1896, **15**, 830.

and calcium are then determined by the ordinary analytical methods. The precipitation of lead with sulphuretted hydrogen must be carried out either in dilute hydrochloric acid solution, or preferably in acetic acid solution, or all the lead may not be precipitated; it is also advisable to weigh the lead as sulphate and not as sulphide. In this way zinc may also be determined in the filtrate from the lead sulphate, as it is likewise precipitated by sulphuretted hydrogen, in acetic acid solution. The precipitation with sulphuretted hydrogen may be entirely avoided, provided the solution does not contain zinc as well as calcium, and sufficient bromine has been added to convert all the lead carbonate into lead peroxide. The black residue consists of lead peroxide and calcium carbonate and is treated with dilute nitric acid, in which calcium carbonate is readily soluble, while lead peroxide is quite insoluble. The latter is then estimated as lead sulphate, by dissolving in hydro chloric acid and evaporating the solution with sulphuric acid. The lead may also be determined volumetrically by placing the filter paper containing the peroxide in a porcelain dish, treating it with about 10 c.c. of dilute nitric acid, adding 20 c.c. of $N/5$ oxalic acid, and heating the solution to boiling; the excess of oxalic acid is titrated back with $N/5$ permanganate solution. One c.c. $N/5$ oxalic acid = 20·71 mg. lead, or 22·29 mg. lead oxide.

The complete analysis of chromium colours, by the method of M. Willenz,[1] is carried out as follows:—One g. of the finely powdered material is treated, with gentle heating, with 100 c.c. of dilute hydrochloric acid (1 : 20), the clear solution filtered off, as much of the insoluble residue as possible being retained in the beaker; the main bulk of the residue, as well as the small portion on the filter paper, is washed with warm water. Calcium and sulphuric acid are estimated in the filtrate, which contains the calcium originally present as carbonate, and calcium sulphate. The residue is digested at the ordinary temperature with 50 c.c. of ammonium acetate solution (sp. gr. 1·04) which should be neutral or slightly alkaline. The solution is then decanted, and the residue washed with warm water as before; lead sulphate goes into solution and is estimated by evaporating the solution to dryness in a weighed platinum dish. After driving off ammonia and acetic acid, the residue is ignited with sulphuric acid. The residue insoluble on treatment with ammonium acetate may contain lead chromate and barium sulphate. It is suspended in 50 c.c. of water, 25 c.c. of potassium hydroxide solution (112 g. per litre) added, and the mixture boiled for about ten minutes; barium sulphate remains unchanged: lead chromate dissolves, forming potassium chromate and potassium plumbate.

In a chrome containing lead sulphate and barium sulphate the

[1] *Bull. Assoc. Belg. des Chim.*, 1898, **12**, 163; *J. Soc. Chem. Ind.*, 1898, **17**, 953.

latter may be estimated by boiling the sample with strong hydrochloric acid, diluting largely, decanting, washing once by decantation and boiling the residue with alkaline ammonium acetate. Barium sulphate remains insoluble.

The total lead in the absence of barium sulphate can be estimated by heating the chrome on a water-bath with strong hydrochloric acid, evaporating to dryness, adding water and dilute sulphuric acid, filtering the lead sulphate and washing with alcohol in the usual way.

Modifications of these processes will suggest themselves in accordance with the results of the qualitative examination.

Examination of Chrome Orange and Chrome Red.—In these colours, besides the examination similar to that of chrome yellow, an estimation of basic lead oxide is also necessary. A finely powdered portion of the colour is treated with acetic acid, whereby basic lead oxide is alone dissolved. The neutral lead chromate, which remains insoluble, is dried and weighed, and the basic lead oxide estimated by difference.

Fastness to Light. The chrome yellows are far less fast to light than zinc yellow, baryta yellow, and strontium yellow. The more unstable, with few exceptions, are the lemon-coloured and pale golden yellow varieties, whereas the chrome oranges are much more permanent in light. The chrome reds are more sensitive to light than the best chrome oranges. Within seven months marked changes have been observed, though some chrome oranges withstand exposure to light for fourteen months without showing much darkening. The palest varieties assume a dirty green appearance; the chrome oranges become greenish-yellow with a brownish tint, and the chrome reds blacken like the cinnabars. The action of light in many lemon-yellow varieties is distinctly noticeable after only four to five days. Oil vehicles form no protection against the action of light on chrome yellows. Church regards the action of light as causing a reduction to green chromic oxide.[1] According to Eder,[2] the brown chromium chromate or dioxide, $CrO_2 . Cr_2O_4$, or $Cr_2O_3 . CrO_3$, is formed.

Behaviour in Mixtures (Fastness to Zinc White). The change which mixtures of cadmium yellow with chrome yellow undergo has already been mentioned. Mixtures of cobalt greens and chrome yellow change colour after a year, becoming brownish-green. In both instances the change is probably due to a partial reduction of the chromate. All chrome yellow pigments are incompatible with lime, since they become converted into basic chromates. The accelerating influence of zinc white on the fading of pigments in the light is particularly noticeable in the chrome yellows. Fifty per cent. mixtures of zinc white with chrome lemon-yellow and chrome golden-yellow of known

[1] *The Chemistry of Paints and Painting*, p. 182. [2] *Photochemie*, p. 175.

fastness to light, were rendered more intensely brown in fifteen days (autumn) than the same pigments without zinc white in seven months. The sensitiveness of chrome yellow towards hydrogen sulphide is well known. Since, at the same time, the chromic acid radical is also partially reduced, the discoloration cannot be completely removed by exposure to light. The chrome yellows are more stable towards sulphur dioxide than the zinc yellows.

Analyses of "Pure" Chrome Colours.

	Pure Primrose Chrome.	Light Chrome.	Pure Pale Chrome.	Pure Middle Chrome.	Pure Deep Chrome.	Deep Orange Chrome.	Pure Orange Chrome.	Pure Scarlet Chrome.	Chinese Red.	Deep Vermilion.
H_2O and volatile matter . .	6·90	0·04	2·48	1·85	5·64	0·03	3·62	1·27	1·69	0·15
$PbCrO_4$ . . .	56·07	68·65	55·30	87·83	73·32	40·56	60·31	59·67	57·55	53·60
$2PbO + Pb(OH)_2$.	0·52	...	11·72	1·32	8·37	47·24	35·48	39·47	39·99 (PbO)	40·88
$PbSO_4$ . . .	36·51	31·21	30·30	8·45	11·98	5·49	...	...	...	4·97
Organic colour .	...	...	...	...	...	4·87	...	...	...	...

Zinc Yellows.

(Zinc Chrome; Lemon-Yellow.)

Zinc yellow, unlike chrome yellow, cannot be obtained in different shades, as zinc does not form differently coloured basic chromates. On the other hand, the tone of zinc yellow is a very pure, delicate but fiery yellow, free from any reddish tint. In consequence, it forms mixed tones of purer green than chrome yellow, and is chiefly used for the production of *Zinc greens* (green cinnabars). It is now prepared exclusively from zinc white, only the best qualities of the latter, the so-called "snow white" or zinc white "green seal," being used. According to Murdoch (1847), the zinc white is treated with a definite quantity of concentrated sulphuric acid, and partially converted into zinc sulphate; a solution containing the calculated amount of potassium bichromate is then added. The zinc yellow obtained in this way is not pure zinc chromate, but the double salt $3(ZnCrO_4).K_2Cr_2O_7$, precipitated on the unchanged zinc oxide. It is, therefore, a substratum pigment.[1]

L. Vanino and F. Ziegler[2] conclude that normal zinc chromate, $ZnCrO_4$, is first formed on mixing the solutions and that this hydrolyses on being washed, giving a more stable basic chromate, approximating to the formula $2K_2O, 3ZnO, 2ZnCrO_4$. According

[1] L. Brock, *Kolloid-Z.*, 1917, **20**, 145. [2] *Chem. Zeit.*, 1925, **49**, 266.

to L. Bock[1] the permanency and tone of zinc yellow depend on its amorphous structure.

Zinc yellow is not quite insoluble in water, as the double salt is slightly decomposed with the liberation of free potassium chromate.

Analysis. Zinc yellow is completely soluble in dilute acetic acid without effervescence—effervescence probably denotes presence of whiting or white lead—a white residue means adulteration with barytes, china, clay, etc., and a yellow residue means presence of lead, chrome, or ochre, with possibly one of these whites. All of these would be determined by their special tests.

A quantitative determination of the zinc present is made by boiling the sample with a large excess of pure sodium carbonate, when total decomposition takes place, the chromic acid being converted into sodium chromate and the zinc remaining as basic carbonate. The latter is filtered off, thoroughly washed, dried, and ignited to ZnO.

Chromic acid is determined as in the lead chromes, by the potassium bichromate and ferrous ammonium sulphate method, using dilute sulphuric acid instead of hydrochloric acid, when a complete solution results.

A sample of zinc chrome analysed by N. Heaton had the composition :—

Water	16·08
Zinc chromate	38·99
Zinc oxide	44·93
	100·00

Fastness to Light and Air. Zinc yellow is to a marked degree more stable to light than the chrome yellows. Water-colour washes exposed to direct sunlight for five years remained unchanged. It is more stable than chrome yellow towards hydrogen sulphide, because the zinc present undergoes no change, and it also appears to be less affected by the reducing action of the gas. On the other hand, like barium yellow and strontium yellow, it is more rapidly attacked by sulphur dioxide than is chrome yellow.[2]

Barium Yellow.

(Yellow Ultramarine; Lemon-Yellow; Permanent Yellow.)

This colour consists of barium chromate. It possesses a much weaker tone than zinc yellow, but its stability in light appears to be greater. Water-colour washes showed no change of tone in five and

[1] *Chem. Zeit.*, 1925, 49, 533.

[2] Zerr and Rübencamp, *Colour Manufacture*, p. 129, state that it is unaffected by sulphurous gases.

a half years. Towards sulphur dioxide, it is more sensitive than the chrome yellows. As a pigment it is of little or no value, its more important application being in the manufacture of matches, where it partly replaces potassium bichromate in making the igniting composition.

Strontium Yellow.

(Yellow Ultramarine; Deep Lemon-Yellow.)

This pigment is strontium chromate. Its shade is more fiery than that of barium yellow. As regards stability to light and other behaviour, it is similar to the latter.

A chromate of calcium is sold under the names of *Steinbühl Yellow*, *Gelbin*, *Yellow Ultramarine*, but barium yellow also frequently passes under these names.

Compatibility in Mixtures. All the yellow chrome colours mentioned, including zinc yellow, are incompatible with white lead as they react with it to form basic chromates, and the tone of the mixture, therefore, becomes reddish after a time. Moreover their instability as chromates comes into play in mixtures with zinc white, Naples yellow, cobalt blue, cœruleum, ultramarine, and cobalt green. The reactions which take place are not yet satisfactorily explained.

Zinc yellow, strontium yellow, and barium yellow, when made up with zinc white into pale-coloured mixtures and used as water colours, are also unstable in direct sunlight. One per cent. mixtures of these pigments faded very considerably in two months (October to December).

V. Red Pigments.

(a) Naturally occurring Red Pigments.

Red Ochres and other Red Mineral Colours.

These colours are essentially naturally burnt ochres containing varying quantities of iron. They have been known and used from the earliest times under such names as *Rubrica*, *Sinopis*, *Armenian bole*, *Lemnos earth*, etc., and occur chiefly in volcanic districts. Their application at the present day is more limited than that of the artificial red iron colours. Deposits are found in Italy (Treviso, Pozzuoli), France, England, Bohemia, the Harz Mountains, Hesse-Nassau, near Saalfeld, etc. This class includes Raddle (red chalk) or red bole, crude red iron-stone, and micaceous iron. The two last-named materials must be calcined, etc., before they can be used for the preparation of paints. Indian red is a natural hæmatite of a purplish-red colour,

containing 95 per cent. of ferric oxide. Venetian red is a brighter natural red hæmatite, and certain hydrated varieties from Tuscany and the Banat (Yugoslavia) are also very bright red.

Red Bole occurs in Armenia, also in Lemnos, Malta, Hungary, Saxony, Silesia, near Wunsiedel, etc., and is a fairly pure clay coloured by ferric oxide. The burnt product comes on to the market as *Stone red*, etc., and was used in the seventeenth and eighteenth centuries as a basis for pastel painting.

Pozzuoli Earth is a volcanic red earth found at Pozzuoli in the neighbourhood of Naples. In the purest form it is almost white or yellowish, but it may possess a reddish to flesh-pink colour owing to the presence of iron. It differs from the ochres and forms a kind of natural cement (Travertine) consisting of partly decomposed clay. It is decomposed by hydrochloric acid, and unlike the ordinary red clays, it contains, besides alumina, lime, magnesia and potassium and sodium as essential components. In this respect it differs from the imitation Pozzuoli earths, which are frequently prepared on account of the high price of the genuine substance, and which are mixtures of English red, etc., and chalk. Genuine Pozzuoli earth, unlike these products, does not effervesce on treatment with acids.

(*b*) Artificial Products.

Commercial Names. Berlin red, blood-red, brown-red, caput mortuum, chemical red, pale, dark and violet oxide of iron, iron saffron, angel red, English red, Indian red, Imperial red, Nuremberg red, Persian red, rouge, Pompeian red, Prague red, Prussian red, red oxide, scarlet-red, Venetian red.

All these substances contain ferric oxide as the chief constituent, and varying quantities of natural argillaceous components. Iron colours prepared from pyrites cinder and sludge mostly contain copper. The chief raw materials are red iron ore, hæmatite, iron ochre, bog iron ore and limonite. Besides these there are certain artificial and waste products such as copperas, pyrites cinder, alum sludge and the vitriol sludge obtained in the manufacture of copper sulphate.

Red Oxide, which serves as a substitute for red lead, is prepared from the foregoing iron ores by calcining them in a reverberatory furnace. By this process the denser ores become porous and the earthy ores are rendered denser and more brittle. Red oxide contains from 82-88 per cent. of ferric oxide, and is a fine brownish- to bluish-red powder possessed of very considerable covering power and the greatest resistance to climatic influences. As an oil colour it protects iron objects effectively against rust. It is free from sulphuric acid, cheaper than red lead, and non-poisonous. The varieties prepared from pyrites cinder may contain sulphur.

The value of red oxide depends on the amount of ferric oxide it contains, and also on the temperature at which it has been roasted. At higher temperatures the amount of ferric oxide increases, without its solubility in hydrochloric acid becoming less; at the same time the specific gravity increases. If heavy adulterants, which can easily be recognised by qualitative analysis, are absent, the specific gravity thus provides a means of estimating the temperature of roasting. Keeping in view chemical properties and cost, a material of sp. gr. 4·2 would best meet practical requirements. Ability to withstand the action of acids and weather increases with an increase in specific gravity, and is determined by a boiling test with dilute acids. Reduction of the substance to a finer state of division increases its covering power, but does not lessen its stability towards acids. The latter is entirely dependent on the temperature employed in the manufacture.[1]

English Red.

(Prussian Red; Venetian Red; Italian Red; Rouge; Colcothar.)

Under these designations red ferric oxide colours, varying in tone from pale yellowish-red to bluish-red, come into the market. They are prepared chiefly from alum or vitriol sludge. Their principal industrial application is as lime and cement colours, but they are also manufactured as artists' colours. As they frequently contain sulphates, they are, on this account, less suitable than red oxide for painting on iron. Owing to its extraordinary colouring power, English red is frequently "let down" with comparatively large amounts of adjuncts, chiefly gypsum (up to 80 per cent.). Gypsum may be already present, however, in the raw materials, or it may be formed during the roasting process from any chalk which is present. If the added gypsum has been previously burnt, the English red becomes lumpy and thickens when used as a water colour.

It is well known that English red, in a similar manner to zinc white, affects the fastness to light of a series of organic colours such as indigo (Church) and especially the coal-tar pigments.

Caput Mortuum. The oldest method of manufacturing this substance is by the calcination of ferrous sulphate. At a later period the Pilsen vitriol schists were used for this purpose. The residue obtained after calcination was formerly ground, and sold, but at the present day it forms the raw material for the manufacture of valuable colours possessing various shades, which are prepared by grinding it with increasing amounts of common salt, and heating again up to definite temperatures in reverberatory furnaces. The duration of this calcining process plays an important part. Yellowish-red shades are obtained with 2 per cent., brownish with 4 per cent., and violet with 6 per cent. of salt.

[1] *Cf.* H. Baucke, *Z. anal. Chem.*, 1898, **37**, 668; *J. Soc. Chem. Ind.*, 1899, **18**, 52.

According to B. Wöhler and Condrea the colour of the different kinds of caput mortuum is also dependent on the size of grain, and can therefore be altered by reduction of the latter.

All the red artificial iron colours are characterised by great colouring and covering power. In the case of those varieties which are used as grinding and polishing media (polishing rouge), hardness, together with fineness of grain, is of the greatest importance.

Velvet Red is a reddish-brown powder consisting of ferric oxide coloured by a mixture of "spirit-soluble" rosaniline blue and fuchsine.[1]

Up to a comparatively recent period English red and caput mortuum colours were frequently "improved" by means of coal-tar dyes. These are detected by placing a portion of the colour on filter paper and moistening it with water, alcohol, or a mixture of alcohol and acetic acid, or by boiling with this mixture and filtering.

Analysis. The estimation of moisture in ferric oxide colours is carried out by drying the colours at 110° until the weight is constant. Further loss on ignition is calculated as water of hydration, provided no sulphates are present. Iron colours become more difficultly soluble in acids the more strongly they are ignited, and the more silica they contain. For the purpose of estimating the contained iron it is best to fuse them with sodium carbonate. The pale varieties of English red dissolve on continued boiling in concentrated hydrochloric acid or aqua regia. Accessory components to be considered are manganese, alumina, magnesium, calcium, and silica.

Small quantities of gypsum, if present, are estimated by determining the amount of sulphuric acid in the acid solution after separation of the iron, aluminium, and manganese. If larger quantities are present the substance is extracted with a hot solution of sodium carbonate, and the amount of sulphate in the extract is determined. The estimation of basic ferric sulphates, which may be present in colours prepared from pyrites cinder and containing gypsum as well, cannot be carried out by this method.

Indian Reds, Red Oxides (Princes Metallic, Tuscan Red, Venetian Red).[2]

Loss at 100°. Two g. is heated in a steam jacketed oven at atmospheric pressure for three hours or to constant weight.

Loss on Ignition. A portion is ignited in a closed porcelain crucible to constant weight. The loss may include combined water, carbon dioxide, organic matter and some sulphur trioxide if much calcium sulphate is present. Carbon dioxide may be determined on a separate portion of the sample if desired.

Free Acid or Alkali. Ten g. of the sample is boiled with 100 c.c. of

[1] *Dingl. polyt. J.*, 1898, 308, 155.

[2] *A.S.T.M. Standards*, 1918, p. 656.

water, filtered and washed. The filtrate is tested with litmus paper, and if acid it is titrated with standard alkali and methyl orange, and calculated to H_2SO_4. If alkaline, it is titrated with acid and calculated to Na_2O. The filtrate is tested for salts of alkalis and of alkaline earths.

Added colouring matter is tested for as on p. 469.

Insoluble Matter, Iron Oxide, etc. Previous roasting at a low temperature is necessary if much organic matter is present; if very low in carbonaceous matter, a little potassium or sodium chlorate may be used in effecting solution. 2·5 g. of the sample is digested with 25 c.c. of hydrochloric acid (adding a little nitric acid or chlorate if not already added). The cover is washed down and the liquid evaporated to dryness. The residue is taken up with hydrochloric acid and water, filtered, washed with dilute hydrochloric acid and water. The filtrate is made up to 500 c.c., mixed and examined as below (for more exact work this should be evaporated to dryness and silica removed). The residue is ignited and weighed as insoluble matter; if the insoluble matter contains an appreciable amount of iron it is necessary to fuse it with sodium carbonate or potassium pyrosulphate to determine the total iron in the sample. If the insoluble matter contains barium sulphate it may be determined by fusing with six times its weight of sodium carbonate, cooling, digesting with hot water, filtering and washing the residue with hot water until free from sulphate. The filtrate is removed and the beaker used for digestion placed underneath the funnel, the filter is then pierced with a glass rod, and the residue washed with a little water into the beaker. Hot dilute hydrochloric acid (1 : 1) is poured over the paper and the whole finally washed with hot water. If necessary more hydrochloric acid is added to the beaker to dissolve the barium carbonate. After heating to boiling, dilute sulphuric acid is added in slight excess, and the beaker is allowed to stand for about one hour on a steam-bath. The precipitate is then filtered, washed, dried, ignited and the barium sulphate weighed. This subtracted from the total insoluble gives the insoluble siliceous matter, if it is desired so to report. If it is desirable to analyse the insoluble siliceous matter, this can be done by the usual methods of silicate analysis, but the results should be reported as a separate analysis.

For the determination of *iron*, 100 c.c. of the first filtrate is placed in a flask, about 3 g. of granulated zinc added, a funnel put into the neck of the flask, and heat applied when the action slackens. If basic salts separate out, a few drops of hydrochloric acid may be added. When the reduction is complete, and as soon as the residual zinc is dissolved, the funnel is washed down, inside and out (and also the neck of the flask) with a fine jet of water. After the flask, which should hold 1 litre, is filled about two-thirds full, it is cooled in water and 10 c.c. of "titrating solution" added. (This made by dissolving 160 g. of

manganese sulphate in water, diluting to 1750 c.c., adding 330 c.c. of phosphoric acid (sp. gr. 1·72) and 320 c.c. of sulphuric acid.) The reduced iron solution is then titrated with potassium permanganate (5·659 g. per litre) which has been standardised against sodium oxalate. A blank is run on the zinc, the result corrected, and the total iron calculated as Fe_2O_3. Instead of adding zinc to the solution, the solution may be reduced in a zinc reductor[1] (p. 75).

Lime. An aliquot of 100 c.c. of the original solution is diluted to about 200 c.c., and 10 c.c. of hydrochloric acid added. It is made alkaline with ammonia, 2 or 3 c.c. of bromine water added, and then boiled till excess of ammonia is expelled. The precipitate is allowed to settle, washed by decantation, redissolved in hydrochloric acid, and reprecipitated with ammonia and bromine water. (Precipitate: Fe_2O_3, Al_2O_3, TiO_2, P_2O_5, MnO_2.) This precipitate may be ignited and weighed if desired. A few drops of ammonia are added to the combined filtrate, which is then heated to boiling, and an excess of saturated ammonium oxalate solution added. The boiling is continued until the precipitate becomes granular, the mixture allowed to stand for about thirty minutes, filtered, and the precipitate washed with hot water until free from ammonium oxalate; (for more exact work this precipitate should be dissolved in hydrochloric acid and the calcium oxalate reprecipitated as above). The precipitate is dissolved in warm dilute sulphuric acid (1 : 4) and then titrated with standard potassium permanganate. If desired, magnesium may be determined as $Mg_2P_2O_7$ in the usual manner in the filtrate from the calcium oxalate.

Soluble Sulphates. One g. of the pigment (if low in insoluble sulphates a larger portion) is roasted gently if much organic matter is present, and then treated with 30 c.c. of hydrochloric acid, boiled for ten minutes, when about 50 c.c. of water is added. Finally the liquid is boiled, filtered, and the insoluble matter washed with water. The solution is heated to boiling, ammonia is added, then the whole filtered and washed a few times with hot water. The precipitate is dissolved in hot dilute hydrochloric acid, reprecipitated with ammonia, then washed well with hot water. The united filtrates are rendered just acid with hydrochloric acid, boiled and precipitated with excess of 10 per cent. barium chloride, and the $BaSO_4$ weighed. The result is calculated to SO_3 or $CaSO_4$.

Total Sulphur other than that present as Barium Sulphate. Five g. of the sample is treated in a covered porcelain dish with 50 c.c. of aqua regia ($1HNO_3 : 9HCl$) and evaporated to dryness on a steam-bath. Twenty c.c. of concentrated hydrochloric acid and about 250 c.c. of water are added, and a double ammonia precipitation made. The sulphur is determined as $BaSO_4$ as above, under "Soluble Sulphates."

[1] Lord and Demorest, *Metallurgical Analysis*, 1913, 28.

Venetian red may be analysed as above. The insoluble matter may be treated with hydrofluoric and sulphuric acids to determine silica by loss.

In the examination of polishing rouge by A. Munkert's method,[1] 2 g. of the substance is boiled for some time with concentrated hydrochloric acid until the oxide of iron is completely dissolved; the solution is evaporated to dryness, the residue taken up with acid, and the solution filtered off from insoluble mineral matter. The filtrate is made up to 250 c.c., and 50 c.c. are used for estimating the sulphuric acid, after precipitation of the iron with ammonia. In a further 50 c.c., iron, aluminium, calcium, and magnesium are determined. Copper is estimated by decomposing 10 g. of the substance with concentrated hydrochloric acid, filtering off the insoluble residue, and reducing the ferric chloride solution with sodium hypophosphite in presence of excess of acid; the copper is then precipitated by sulphuretted hydrogen, and determined electrolytically.

The microscopic examination of the residue insoluble in acid (any soluble silica present can be removed by sodium carbonate solution) affords valuable evidence as to the nature and condition of the mineral admixtures, and frequently as to the method of manufacture.

Fastness to Light. Artificial ferric oxide colours, provided that they are not "improved" with coal-tar dyes, are quite fast to light and are fully miscible with other colours. On the other hand, all these colours, like the burnt ochres, sienna earths, and umbers, possess the property of being slightly soluble in the usual fatty oils, and this solubility forms one of the causes of the subsequent darkening which they undergo when used as oil paints. English red has been stated to have an injurious effect on coal-tar colours on exposure of the pigments to light, as in the case of zinc white.

Analyses of Indian Reds, Red Oxides, Venetian Reds, and English Red.

	Insoluble and SiO_2.	Fe_2O_3.	Al_2O_3	CaO.	CO_2.	MgO.	SO_3.	Moisture.	Loss on Ignition.
Pure Indian Red	0·67	94·35	2·69	...	...	...	...	0·20	1·53
Red Oxide	11·55	53·95	12·03	9·33	...	0·68	1·55	0·01	10·95
Turkey Red Oxide	15·74	64·00	6·15	5·88	...	0·48	0·20	0·06	7·25
Royal Venetian Red	1·82	9·00	0·57	30·47	39·40	18·26	...	0·30	...
Venetian Red	1·07	9·50	0·28	45·00	12·06	0·50	25·00	6·84	...
Rouge	...	82·25	...	...	...	...	...	7·35	10·40
English Red	11·35	78·4	2·3	3·0	...	...	0·60	Water 4·35	
Purple Oxide	1·2	98·5	...	...	...	...	...	...	0·3

[1] *Z. angew. Chem.*, 1900, **13**, 593; *J. Soc. Chem. Ind.*, 1900, **19**, 672.

Red Lead (Minium).

Red lead is prepared on a manufacturing scale (*a*) by calcining lead oxide (PbO) in the form of massicot (not litharge[1]) in muffle furnaces into which air is admitted. The commercial product obtained in this way is known under the name of "Crystal minium" or "true red lead." (*b*) By calcining powdered white lead. The red lead obtained by the second process is of finer grain, warmer in tone and dearer than crystal minium, and is called "Orange lead." It also possesses greater covering power than the other brand. Crystal red lead is chiefly used as an oil colour, as a priming in painting on iron, as a packing material for joints in machinery, and for the preparation of red lead putty. The finer orange lead serves chiefly as a pigment, and when used as an artist's colour it is known as "Saturn red." (*c*) In this method lead sulphate is mixed with sodium carbonate and sodium nitrate and the mixture heated to a dull red heat. This method of preparation is now very little used.

Red lead has the approximate composition Pb_3O_4 or [2(PbO). PbO_2].

Copper, bismuth, iron, and antimony have an injurious effect on the colour of red lead.[2]

The British Standard specification for red lead makes provision for two grades (A and B), A being ordinary quality for paint purposes and containing not less than 72 per cent. Pb_3O_4 and B for jointing purposes, with not less than 43 per cent. and not more than 72 per cent. Pb_3O_4. In both grades not less than 99·5 per cent. of lead oxides must be present.[3]

An account of the preparation, properties, and decomposition of red lead has been published by J. Milbauer.[4] Reference may also be made to A. H. Sabin, *Red Lead and how to use it in Paint*, 1920.

"New process" lead oxide, obtained by violent agitation of molten lead in cast-iron containers in a current of air, is brown to yellow in colour, and may contain 4·7 per cent. metallic lead. Sublimed oxide, an American product, is obtained by oxidising lead and subliming the resultant oxide, using natural gas as a source of heat. Orange lead differs from red lead in its higher content of PbO_2, the theoretical proportion of 34·94 per cent., however, never being attained. It is suggested by Klein[5] that Pb_3O_4 possibly consists of a solid solution of PbO and PbO_2.

[1] *Cf.* Zerr and Rübencamp, *Colour Manufacture*, p. 259.

[2] O. Herting, *Chem. Zeit.*, 1903, **27**, 923; *J. Soc. Chem. Ind.*, 1903, **22**, 1138.

[3] *B.E.S.A.*, 1926, Specification No. 217.

[4] *Physikalische, chemische und technische Studien über die Mennige: Chem. Zeit.*, 1909, **33**, 513, 522, 950, 960; 1910, **34**, 138, 1341; *J. Soc. Chem. Ind.*, 1909, **28**, 612, 1049; 1910, **29**, 282; 1911, **30**, 37.

[5] *J. Soc. Chem. Ind.*, 1919, **38**, 471A.

According to Bolley-Stahlschmidt,[1] litharge is impure lead oxide while massicot is the almost pure substance. Zerr and Rübencamp consider that the differences between the two substances lie in their physical condition. Litharge is to be looked upon as fused crystalline lead oxide. Owing to its density it can be further oxidised only with great difficulty; hence it is not suitable for the manufacture of red lead On the other hand, massicot, a very delicate pale yellow powder, is very readily oxidised in the air. Both products should dissolve completely in nitric acid, and all the lead should be precipitated out of the solution by sulphuric acid, so that, on complete evaporation of the liquid remaining after filtration from the precipitate, only a minute residue should remain. The presence of calcium salts may be detected by dissolving in dilute nitric acid, excess being avoided; the solution is then diluted with water, and sulphuretted hydrogen passed in until it smells strongly of the latter. The precipitate is filtered off, and the filtrate treated with ammonia and ammonium oxalate. Evolution of carbon dioxide, on addition of acid, indicates the presence of calcium carbonate or lead carbonate—the latter if no calcium salts have been found by the previous test. Carbon dioxide is estimated in an ordinary Schrötter or similar apparatus. Particles of earth, brick dust, raddle and red ochre are either insoluble in nitric acid or are found in the solution after precipitation of the lead by sulphuric acid; the same holds good for ferric oxide, which is often present in litharge. Stannic oxide remains in the residue insoluble in nitric acid, but is seldom contained in any considerable quantity in litharge. Copper is detected by digesting a small portion of the sample with ammonia, a blue coloration being obtained when the metal is present to any considerable extent. Litharge and red lead, when used in the manufacture of glass, must be quite free from copper and ferric oxides.[2] According to T. Salzer,[3] nitrous acid and gypsum are occasionally found in litharge.

The Analysis of Red Lead. A. *Examination for Impurities.* Red lead becomes dark violet to black when heated; on cooling it returns to its original hue. It is soluble in glacial acetic acid; and in a mixture of nitric acid with reducing agents. Of the latter, oxalic acid or sugar used to be used; lactic acid (A. Partheil[4]) avoids the formation of lead oxalate, while L. Opificius[5] uses metallic copper, and J. F. Sacher[6] uses formaldehyde. Hydrogen peroxide is now usually employed (F. P. Dunnington[7] and P. Beck[8]). Adulterants such as brick dust, ferric oxide, heavy spar, etc., which remain undissolved, are thus

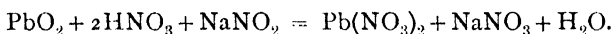
[1] *Handbuch der chem. techn. Untersuchungen*, 6th ed., p. 355.
[2] *Cf.* the section on "Glass," Vol. III.
[3] *Pharm. Zentr.*, 1889, **29**, 645; *Z. anal. Chem.*, 1889, **28**, 734.
[4] *Chem. Zeit.*, 1907, **31**, 941.
[5] *Ibid.*, 1888, **12**, 477.
[6] *Chem. Zeit.*, 1908, **32**, 62; *J. Soc. Chem. Ind.*, 1908, **27**, 169.
[7] *Z. anal. Chem.*, 1889, **28**, 338.
[8] *Z. anal. Chem.*, 1908, **47**, 465.

detected. This method can also be used in the estimation of the insoluble residue in red lead which has been "let down" with barium sulphate. Dilute nitric acid and aqueous acetic acid form lead salts, and at the same time lead peroxide separates out. Dilute hydrochloric acid acts similarly. With excess of concentrated hydrochloric acid, lead chloride is formed and chlorine evolved. Concentrated sulphuric acid decomposes red lead with evolution of oxygen and formation of lead sulphate. Sodium hydroxide has no action.

R. Frühling[1] states that the insoluble residue, after treating red lead with dilute nitric acid and sugar solution or hydrogen peroxide, should not amount to more than 1 per cent. if the red lead is to be used for pharmaceutical purposes—*e.g.* for plasters. On the other hand, as much as 10 per cent. is permissible when it is employed in the preparation of oil colours, metal paints, joints in steam pipes, etc.

B. *Estimation of the Content of Lead Peroxide.* (a) *Volumetric Methods.* According to P. Beck, the volumetric method of A. Lux,[2] which depends on the use of *N*/5 oxalic acid and permanganate, and was formerly employed for this purpose, gives less accurate results than the iodometric method of G. Topf and W. Diehl.[3] P. Beck[4] has described a variation of this method, making use of carbon dioxide. An alternative volumetric method is that of M. Liebig, jun.,[5] according to which 0·5 g. of the sample is treated in a small Erlenmeyer flask with 25 c.c. of *N*/10 sodium thiosulphate and 10 c.c. of about 30 per cent. acetic acid, and dissolved by shaking; 10 c.c. of potassium iodide solution (1 : 10) and 2-3 c.c. of zinc iodide starch solution are then added, and the solution titrated with *N*/10 iodine solution. The end of the reaction is sharply indicated by the lemon-yellow colour of lead iodide changing to a dirty dark yellow (*cf.* also p. 502).

E. Szlerkhers[6] uses sodium nitrite, which reacts with PbO_2 according to the following equation:—

$$PbO_2 + 2HNO_3 + NaNO_2 = Pb(NO_3)_2 + NaNO_3 + H_2O.$$

Five g. of red lead is warmed for a quarter of an hour with 100 c.c. of boiling water and 5-7 c.c. of pure nitric acid on the water-bath; the solution is allowed to cool down to 50°, treated, drop by drop, with excess of standardised sodium nitrite solution (about 1 per cent.), and the excess of nitrite titrated back with permanganate solution (0·8 per cent.).

In the course of a critical examination of the various methods,

[1] *Z. angew. Chem.*, 1889, **2**, 68.
[2] *Z. anal. Chem.*, 1880, **19**, 153.
[3] *Ibid.*, 1887, **26**, 296.
[4] *Loc. cit.*
[5] *Z. angew. Chem.*, 1901, **14**, 828; *J. Soc. Chem. Ind.*, 1901, **20**, 1027.
[6] *Ann. Chim. anal.*, 1902, **7**, 214; *J. Soc. Chem. Ind.*, 1902, **21**, 1156.

A. Chwala and H. Colle[1] recommend the following procedure:—1·2 g. of the sample is treated with 100 c.c. of cold $N/1$ nitric acid and 25 c.c. of $N/1$ oxalic acid. The mixture is heated until decomposition is complete, which requires ten to fifteen minutes. The solution is then titrated, at a temperature of 70°-80°, with $N/1$ or $N/5$ permanganate, allowing the main bulk to run in rapidly, and then continuing the titration carefully to the end-point.

J. A. Schaeffer[2] describes a rapid method of analysis of red lead and orange lead depending on the estimation of lead peroxide produced on treatment with nitric acid and subsequent addition of a known quantity of hydrogen peroxide. The excess of hydrogen peroxide is estimated by permanganate. A blank test is made with the same volumes of hydrogen peroxide and nitric acid.

The American standard method[3] of analysis of dry red lead is as follows:—

Specific Gravity. The true specific gravity is determined by Thompson's method, or by means of a 50 c.c. pyknometer, using benzine and 20 g. of pigment.

Moisture. Two g. of the sample is dried for two hours at 105°; the loss in weight is considered as moisture.

Organic Colour. Two g. of the sample is boiled with 25 c.c. of 95 per cent. methyl alcohol, allowed to settle and the supernatant liquid decanted. The residue is boiled with water, decanted as before, and again boiled with very dilute ammonia. If either the alcohol, water, or ammonia is coloured, organic colouring matter is indicated.

Total Lead and Insoluble Matter. One g. of the sample is treated with 15 c.c. of nitric acid (1 : 1) and sufficient hydrogen peroxide to dissolve all lead peroxide on warming. If any insoluble matter is present, 25 c.c. of water is added, and the whole boiled, filtered, and the residue washed with hot water. The insoluble matter contains free silica and should be examined for silicates and barium sulphate if the total quantity is appreciable. To the original solution or filtrate from the insoluble matter 20 c.c. of concentrated sulphuric acid is added and the work proceeded with as under "Basic Carbonate of Lead" (p. 422).

If calcium and magnesium are to be determined the procedure is as follows. The lead is precipitated as sulphide from a slightly acid (hydrochloric acid) solution, the lead sulphide dissolved in hot dilute nitric acid, and the lead determined as sulphate. The filtrates from the lead sulphide are boiled to expel hydrogen sulphide, and a little bromine water added to oxidise the iron (if present). Bromine is expelled by boiling, and ammonia added in slight excess. Any

[1] *Z. anal. Chem.*, 1911, **50**, 209; *J. Soc. Chem. Ind.*, 1911, **30**, 802.
[2] *Ind. Eng. Chem.*, 1916, **8**, 237. [3] *A.S.T.M. Standards*, 1918, 649.

precipitate of ferric hydroxide and aluminium hydroxide is filtered off, and washed with hot water; if appreciable, it is redissolved in hot dilute hydrochloric acid reprecipitated with ammonia, then ignited and weighed as mixed oxides. Manganese (if present) can be precipitated by adding bromine and ammonia, and warming. All the filtrates are united, the whole made slightly acid with acetic acid, then heated to boiling, and hydrogen sulphide passed into the hot solution till saturated. Five g. of ammonium chloride is added and the liquid allowed to stand for five hours, any zinc sulphide is filtered off, washed with sulphuretted hydrogen water, and the zinc sulphide dissolved in hot dilute hydrochloric acid. The zinc is determined by titration with potassium ferrocyanide. Alternatively the sulphuretted hydrogen may be boiled off, any separated sulphur filtered out, and the zinc determined as phosphate. Calcium may be determined in the filtrate from zinc sulphide by expelling sulphuretted hydrogen and then precipitating as oxalate. The magnesium is determined in the filtrate from the calcium in the usual manner by precipitating with sodium phosphate solution.

Lead Peroxide and true Red Lead. One g. of the finely ground sample is weighed into a 200 c.c. Erlenmeyer flask, a few drops of distilled water added, and the mixture rubbed to a smooth paste with a glass rod flattened at the end. Thirty g. of pure crystallised sodium acetate, 2-4 g. of pure potassium iodide, 10 c.c. of water, and 10 c.c. of 50 per cent. acetic acid are mixed in a small beaker and stirred until all is liquid, warming gently. If necessary, 2 or 3 c.c. of water may be added; the liquid is cooled to room temperature and poured into the flask containing the red lead. The sample is rubbed with a glass rod till nearly all the red lead has been dissolved; 30 c.c. of water containing 5 or 6 g. of sodium acetate is added and the mixture titrated at once with $N/10$ sodium thiosulphate, adding the latter rather slowly and keeping the liquid constantly in motion by whirling the flask. When the solution has become light yellow any undissolved particles must be rubbed up with the rod until free iodine no longer forms, then the rod is washed, and sodium thiosulphate solution added until the solution is pale yellow. The liquid is then titrated to the end-point. The iodine value of the sodium thiosulphate solution multiplied by 0·94193. = PbO_2, and multiplied by 2·69973. = Pb_3O_4.

Glasstone[1] criticises this method and recommends the use of hydrochloric acid and sodium chloride instead of acetic acid and sodium acetate to keep the lead iodide in solution.[2]

This method is not applicable when, besides the oxides of lead, other substances are present, which liberate iodine under the conditions given.

[1] *J. Chem. Soc.*, 1921, **119**, 1997.
[2] See also Chwala and Colle, *Z. anal. Chem.*, 1911, **50**, 209.

In the British Standard specification for red lead[1] the following method is recommended:[2]—

"One g. of red lead shall be placed in a glass mortar with 40 c.c. of saturated solution of sodium acetate in 5 per cent. acetic acid, and shall be rubbed with a pestle until thoroughly wetted. A known excess (about 40 to 50 c.c.) of *N*/10 sodium thiosulphate solution shall be then run in and rubbing continued until all the red lead is dissolved, after which a few drops of starch solution shall be added, and the whole titrated with *N*/10 iodine solution.

Note.—The last few milligrammes often require considerable rubbing, and the addition of a little potassium iodide is helpful and does not affect the titration."

Water-soluble material may be alkaline or may contain nitrates, nitrites, carbonates, sulphates, sodium, and lead

Total Silica. Five g. of the sample is digested in a covered casserole with 5 c.c. of hydrochloric acid and 15 c.c. of nitric acid (1 : 1). After evaporating to dryness to dehydrate, cooling, treating with hot water and nitric acid and boiling, the silica is filtered off, washed with hot acidified ammonium acetate solution, then with diluted hydrochloric acid, and finally with hot water. It is then ignited and weighed as SiO_2. The residue may be treated with sulphuric and hydrofluoric acids if its purity is doubtful.

Carbon Dioxide. Carbon dioxide may be determined by the evolution method, using dilute hydrochloric acid and stannous chloride.

Soluble Sulphates. See under Sulphates other than Barium Sulphate under the analysis of Zinc Leads (p. 446).

Iron Oxide. Iron oxide is determined by Schaeffer's modification of Thompson's colorimetric method[3]; or 20 g. of the sample may be treated in a large beaker with 20 c.c. of water 20 c.c. of nitric acid (sp. gr. 1·4), and 3 c.c. of formaldehyde solution. This is then warmed till all the lead peroxide is dissolved, diluted with water and heated; the insoluble matter is filtered off and finally washed with hot water. After ignition the insoluble matter is filtered and evaporated with sulphuric and hydrofluoric acids. Fourteen c.c. of sulphuric acid (1 : 1) is added to the filtrate from insoluble matter, the lead sulphate is filtered off and then washed. The residue from treatment with hydrofluoric and sulphuric acid is dissolved in sulphuric acid and added to the filtrate from lead sulphate, which is then diluted to 500 c.c. and iron determined in an aliquot colorimetrically, using the same amount of nitric acid, sulphuric acid, and formaldehyde in comparison solution.[4] The result is calculated to Fe_2O_3.

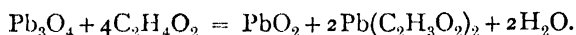
[1] *B.E.S.A.*, 1926, No. 217.

[2] Abstracted by permission of the British Engineering Standards Association, from B.S. specification No. 217, official copies of which can be obtained from the Secretary, 28 Victoria Street, S.W. 1, price 2s. 2d. post free.

[3] *Ind. Eng. Chem.*, 1912, 4, 659.

[4] *Lunge-Berl. Chemische-technische Untersuchungs-Methoden*, 6th Ed., Vol. II., p. 95.

(b) *Gravimetric Method.* For the gravimetric estimation H. Forestier[1] suggests the use of acetic acid, which reacts in accordance with the equation:—

$$Pb_3O_4 + 4C_2H_4O_2 = PbO_2 + 2Pb(C_2H_3O_2)_2 + 2H_2O.$$

One g. of red lead is heated for half an hour with 10 c.c. of 10 per cent. acetic acid and 20 c.c. of distilled water on the water-bath, and the lead peroxide which separates out is estimated either by direct weighing or by titration.

J. F. Tocher[2] recommends the following modification of a method given by Sutton for estimating the amount of peroxide in red lead: 2·064 g. of red lead is treated with 50 c.c. of $N/1$ nitric acid (sp. gr. 1·05) in the cold; PbO dissolves and PbO_2 remains insoluble. If the solution be then heated almost to boiling and 50 c.c. of $N/5$ oxalic acid added, the lead peroxide is nearly all dissolved; the solution is then treated with dilute sulphuric acid and titrated with $N/5$ permanganate until the red coloration is permanent. The number of cubic centimetres of permanganate required, subtracted from 50, gives the percentage of peroxide in the red lead.

The better qualities of red lead, when ignited in a covered crucible, lose from 2·4-2·6 per cent. of oxygen; inferior qualities lose less, down to as little as 1·3 per cent.

The amount of lead peroxide contained in the commercial varieties of red lead varies from 26·32 to 34·89 per cent.

Fastness to Light. Red lead, especially in the form of powder, is not faster to light than vermilion; it becomes black owing to oxidation to lead peroxide. As an oil colour it is much more stable.

Behaviour in Mixtures (Fastness to Zinc White). Red lead is incompatible with copper pigments such as verdigris, and also with the arsenic greens—Schweinfurth green, Scheele's green, etc., when formation of lead peroxide probably takes place. Eight per cent. mixtures of red lead with zinc white as water colours, when exposed to direct sunlight under glass, faded considerably within a month (November).

Of all mineral pigments red lead has the greatest effect on the rate of drying of the fatty drying oils (formation of lead soap). In combination with the oils it forms pastes which rapidly harden and are used, as already mentioned, as packing for making close joints in ironwork, etc.

Artificially coloured Varieties of Red Lead. Cinnabar substitutes made artificially by colouring red lead with eosin or azo-dyes, or by precipitation of the latter on to the mineral colour, were formerly found

[1] *Z. angew. Chem.*, 1898, **11**, 176.
[2] *Pharm. J.*, 1900, **64**, 310; *J. Soc. Chem. Ind.*, 1900, **19**, 471.

on the market, but they have now been almost entirely superseded by superior cinnabar substitutes produced from coal-tar dyes which are fast to water and to oil. (Newer Signal reds.) Amongst the older productions having red lead as a base are the following:—

"*Carminette Yellow*"[1] is a heavy, warm, red powder which, on heating with distilled water, forms a pink solution, having a beautiful green fluorescence. It consists of red lead which is coloured by "eosin extra yellowish."

"*Carminette Blue*" is a similar product, but a shade darker, and consists of red lead coloured with a bluish eosin.

The products known as "Carminette blue-red, reddish-yellow, warm-red and warm-dark," are similarly constituted.

"*Cinnabar Imitation*," or "bluish and yellowish cinnabar substitute," consists likewise of red lead coloured with Rose Bengal or a mixture of this dye with some cochineal scarlet 2R.

Garnet Red,[2] a heavy, warm red powder, is red lead coloured with croceïn, while another quality consists of orange lead coloured with Ponceau 2R and 3R.

These pigments become brown on treatment with dilute nitric acid, and in this way the presence of red lead can be recognised.

Analyses of Coloured Varieties of Red Lead (Holley).

	Vermilion.	Radium Vermilion.
Moisture	0·16	0·06
Red lead	80·08	97·99
Barytes	16·83	...
Alumina	0·77	...
Organic colour	2·16	1·95

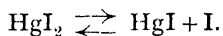
Brilliant Scarlet.

(Iodine Red; Mercury Iodide; Scarlet-Red.)

This pigment, which is only used as an artist's colour, is mercuric iodide. It occurs in nature as the mineral coccinite. Brilliant scarlet is one of the most unreliable of mineral pigments. It is dimorphous. The red modification is the stable form at ordinary temperatures, and when heated, passes into the yellow rhombic form. Both forms are mutually convertible into one another, but the yellow modification seldom changes of its own accord, but passes into the red form when subjected to rubbing, pressing, or on heating below 120°; according to W. Schwarz, the transition temperature of the two forms is 126°·3.

[1] M. Bottler, *Dingl. polyt. J.*, 1898, 308, 153.
[2] *Cf.* M. Bottler, *loc. cit.*

The formation of the red form from the yellow takes place with evolution of heat. When exposed to light it also becomes yellow. When mixed with zinc white it turns blackish-violet even in twenty-four hours (November), and passes later into the yellow modification. The first change is a light reaction which is reversible, and may be looked upon as taking place according to the equation :—

$$HgI_2 \rightleftarrows HgI + I.$$

In contact with metallic iron, mercuric iodide undergoes decomposition with the formation of mercury and ferrous iodide. Brilliant scarlet is recognised by the colour change on heating. Its purity is indicated by a sublimation test, or by dissolving it in potassium iodide.

Vermilion (Cinnabar).

This pigment is mercuric sulphide, HgS. It occurs native as cinnabar, but this form is sold only on a very small scale at the present day, for in beauty of shade it is inferior to the manufactured varieties, particularly to those prepared by the wet method. The principal methods of manufacture are the dry method, in which black mercuric sulphide is first formed and then converted into the red modification by sublimation ; and the wet method, in which at least one of the materials, such as potassium pentasulphide, is used in a dissolved condition.[1] The manufactured products are usually sold as "pale" and "dark" according to their shades. "Carmine cinnabars" are prepared in the wet way. These pigments do not contain English red. The manufacturer's specifications are expressed either by figures or by letters. Under the designation "Chinese vermilion" some particularly warm vermilions of superior fastness to light are sold. Vermilion is the heaviest pigment known (sp. gr. 8·2). It is very opaque and consequently possesses great covering power.

Analysis. Vermilion is quite insoluble in water, alkalis, and any single acid, but soluble in aqua regia. It burns with a pale blue flame when heated in the air, and if pure leaves only a trace of ash.

Metallic mercury, free sulphur and iron are best detected by dissolving the vermilion in potassium monosulphide solution (1 : 1). Brunner observed that the pigment dissolved in this solution with extraordinary ease. When the ferrous sulphide has settled, the solution is colourless. If metallic mercury is present, it settles after some time as a grey cloud. The presence of free sulphur is detected by the yellow coloration of the solution, which, however, disappears in time as the sulphur slowly combines with the potassium monosulphide.

[1] *Cf.* Zerr and Rübencamp, *Colour Manufacture*, p. 274.

Sulphur may also be detected in the usual way, either by digesting with potassium hydroxide or by extracting with carbon bisulphide provided that the sulphur is present in the crystalline state.

The quantitative determination is carried out by extracting with sodium carbonate solution, and then oxidising to sulphate. In order to ascertain the presence of foreign adjuncts such as heavy spar, clay, red lead, chrome red, brick dust, English red, etc., which, however, are very seldom present to-day, the sublimation method was formerly used. In testing qualitatively for these impurities or intentional additions, the use of potassium monosulphide is preferable. After filtration the residue must not be washed with water at first, but with dilute potassium hydroxide solution, as otherwise Brunner's salt ($HgS . K_2S . 5H_2O$), which has been formed, will be decomposed with separation of black mercuric sulphide. Dragon's blood and coal-tar dyes are detected by extracting the sample with alcohol; "carmined" vermilion is recognised by spotting a portion with ammonia on filter paper. These adjuncts, however, are very seldom present nowadays. On the other hand, a "Secondary Vermilion" is manufactured, which consists of vermilion intimately mixed with heavy spar. Arsenic sulphide is recognised by boiling with sodium hydroxide, acidifying with hydrochloric acid, and passing in sulphuretted hydrogen. Combined sulphur is estimated, according to P. Jannasch and H. Lehnert,[1] by burning the vermilion in a current of oxygen and collecting the volatile products in hydrogen peroxide. The mercury which comes over is dissolved by adding aqua regia, the solution evaporated to dryness, the residue taken up with water and hydrochloric acid, and the sulphate formed precipitated with barium chloride.

Hue and Fastness to Light. Vermilions prepared in the wet way exhibit a much greater variety of shade than those manufactured by the sublimation process, and also possess greater brilliance. By the wet method colours ranging from bright warm orange to dark dull blue-red are obtained. Both a light and a dark variety are nearly always obtained together as the products of one single process of preparation; they can be separated by levigation. These differences of colour depend on size of grain, as in the oxides of mercury, oxides of iron, etc.

According to Church[2] and A. W. Keim,[3] the palest artificial vermilions are the most unstable to light. A. Eibner observed, on the contrary, in one hundred and eight individual tests, that, of the vermilions manufactured in the wet way, the darker bluish-tinged and medium shades darkened much more intensely than the palest varieties

[1] *Z. anorg. Chem.*, 1896, **12**, 129.
[2] *The Chemistry of Paints and Painting*, p. 189.
[3] *Techn. Mitt. f. Malerei*, 1907, **23**, 212.

within the same period of time. The sensitiveness to light of artificial vermilion is, therefore, not proportional to the fineness of grain. The vermilions most fugitive in light are found amongst those prepared by the wet process. Out of fifty kinds, including three prepared in the dry way, 30 per cent. darkened very distinctly within four to five days. Out of fifty-eight samples of vermilion (of German and Austrian origin); mostly prepared in the wet way, only 30 per cent. remained unchanged during a period of six months; amongst these were those manufactured by the dry process, and the native vermilions. After a year, only the sublimed and the native products showed very little or no change. It was observed in certain carmine vermilions that the first signs of darkening on exposure to light diminished again in the dark, until the original shade was restored. Thus this light reaction also appears to be reversible as far as the first stage is concerned. If the darkening effect once becomes stronger, then the reaction begins to be irreversible. (*Cf.* Prussian blue.) As a general rule the darkening of vermilion in the light takes place superficially.

These phenomena have not yet been clearly explained. They depend either on the effect of the vehicles employed, or on the presence of a modification of vermilion transformable with particular ease at the points affected. With regard to the former of these suggested explanations, the statement by Alsberg that vermilion rapidly becomes black when steam is passed over it, is of importance, and von Heumann has observed that this accelerating effect is also produced by ammonia and alkalis. Von Heumann also showed that when vermilion is rubbed on a sheet of copper the latter is blackened, copper sulphide being formed.

Behaviour in Mixtures (*Fastness to Zinc White*). The numerous statements which have been made with regard to the double decomposition of vermilion with white lead and other lead colours are in error, so far as technically pure mercuric sulphide is concerned. Experiments have shown that:—(1) Vermilions containing free sulphur or alkali sulphides turn to a dark brownish-red when boiled with lead acetate solution, and also when warmed with pure white lead free from lead acetate. (2) Vermilions from which the sulphur has been extracted retain their colour when treated in the same manner. Mixtures of pure vermilions and pure white lead made into a thin paste with water, and allowed to settle, did not change colour during a year. After three years they had darkened superficially, but only through the transformation of the vermilion into the black modification. Oil washes of mixtures of the pure pigments, kept in the dark, remained unchanged for six years.

The darkening of cinnabar in the light is not arrested by mixing it with white lead, zinc white, whiting, lithopone, or barium sulphate.

Zinc white has, to a certain extent, a special effect. Washes made up from pale zinc white mixtures and gum arabic become distinctly grey within fourteen days, a change also observed in mixtures prepared with the other white pigments. Subsequently, however, the zinc white mixtures fade quite distinctly, apparently owing to oxidation of the vermilion.

Imitation Vermilions. (See under Red Lead, p. 504.) A series of new coal-tar dyes of relatively high permanence in light (permanent reds, etc.) has rendered it possible to manufacture vermilion substitutes for painting signal colours, and for colour printing, wallpaper printing, etc., which, as regards fastness to light, fully satisfy requirements, and naturally do not exhibit the property of blackening. Among the mineral colours pale cadmium red in oil appears to be coming into vogue as a vermilion substitute, chiefly for artists' use.

Antimony Vermilion.

This pigment has lost its former importance in painting chiefly on account of the fact that the method of preparation is relatively complicated and the desired shade is not always obtained. The Mathieu Plessy process consists in precipitating a solution of antimony chloride with a solution of sodium thiosulphate; in the Wagner's process tartar emetic, tartaric acid, and thiosulphate are used. When properly prepared it possesses a pure red colour without any yellow or blue tinge but with a tendency towards a brown tint. When heated with sodium carbonate solution or lime water it darkens strongly, and is, therefore, not fast to lime. When boiled with potassium or sodium hydroxide it dissolves and is reprecipitated on addition of an acid; when heated it blackens but does not sublime, and thus differs from vermilion. It is dissolved by boiling with strong hydrochloric acid with evolution of sulphuretted hydrogen. If iron oxide is present it gives a yellow colour to the acid solution, while chrome orange imparts to it a green colour—these adulterations are confirmed by the usual tests. The vermilion darkens on addition of hydrochloric acid if red lead is present and after boiling and cooling, crystals of lead chloride separate out. According to Mierzinski,[1] antimony vermilion is fast to light and air. By carrying out the precipitation of antimony solutions with thiosulphate in the presence of alum, P. J. F. Souviron[2] claims to obtain red antimony sulphide pigments of improved colour and stability.

[1] *Handb. der Farbenfabrikation*, vol. i., p. 516.

[2] Fr. Pat., 600894.

Cadmium Scarlet.

This pigment is recognised by the colour of its powder, which differs from the very deep cadmium orange to which the name "cadmium red" is sometimes given. At present it is sold in two shades, viz., pale and dark cadmium red. Both varieties form dull powders of a colour somewhat resembling that of Pozzuoli earth, but when ground in oil they produce red tones of such warmth that these colours are now employed as vermilion substitutes and as artists' oil colours.

According to Eibner,[1] both varieties of the older cadmium red contain preponderating amounts of cadmium sulphide and small quantities of cadmium selenide, and, in addition, heavy spar as a diluent. The cadmium selenide is the component responsible for the shades of these colours. It is not yet known in what way these pure red shades, free from any yellow tint, originate; it may be assumed, however, that a chemical compound, an isomorphous mixture, or a solid solution of cadmium sulphide and cadmium selenide is present, and not merely a mechanical mixture. Experiments have shown that the heavy spar in these colours is in all probability present not as an adulterant, but as a substratum without which the shades could not be produced. Pure cadmium-selenium sulphide somewhat resembles caput mortuum in colour. The pale varieties of this kind of cadmium red contain about 76 per cent., the dark about 58 per cent. of barium sulphate. The most recent products of this nature contain no heavy spar, and in these the excess of cadmium yellow acts as the substratum According to the choice of substratum and the quantity of selenium present, shades varying from red to purple can be produced. Cadmium red cannot be employed as a water colour or distemper, since in these vehicles the necessary deepening in shade of the powdered pigment is not developed. Reference may be made to H. Dudley Ward's paper on Cadmium pigments.[2]

Qualitative Analysis. On warming the cadmium red colours with dilute hydrochloric acid, sulphuretted hydrogen is first liberated; the colour then becomes dirty red and subsequently grey, and at the same time the horse-radish odour of the highly poisonous selenium hydride is noticeable. This compound is also detected by the appearance of white clouds of selenious acid on igniting the gas. If the gas is passed into water or into aqueous sulphurous acid, red selenium separates out. On continued boiling, the pigment either dissolves, leaving only the insoluble heavy spar, or else selenium in the form of a grey powder remains with the latter. The varieties which contain no heavy spar leave behind only traces of selenium.

[1] *Malmaterialienkunde*, p. 143. [2] *J. Oil and Col. Chem. Assoc.*, 1927, 10, 4.

Quantitative Analysis. Sulphur and Insoluble Matter. One g. of the pigment is heated with concentrated nitric acid until colourless, the solution diluted with distilled water, and, after standing, filtered from insoluble barium sulphate, which is weighed. The filtrate is evaporated with hydrochloric acid to expel nitric acid and diluted with distilled water. The oxidised sulphides are then estimated by precipitation with barium chloride in the usual manner.

Selenium.—0·5 g. of the pigment is treated with concentrated nitric acid as before and filtered from insoluble matter. The filtrate is evaporated with hydrochloric acid, several operations being necessary to effect complete removal of nitric acid, during which process loss of selenium by volatilisation is prevented by the addition of alkali chloride. The liquid, which should contain at least 30 per cent. of its volume of concentrated hydrochloric acid, is treated with sulphur dioxide or sodium bisulphite at boiling heat for fifteen minutes, whereby the red precipitate of selenium first formed is converted into the black modification which is easier to filter and wash. The filtrate is again reduced to ensure complete precipitation and the precipitate is collected on a tared Gooch crucible, dried at 105° and weighed as selenium.

Cadmium. The filtrate from the selenium is boiled to expel the sulphurous acid, ammonia added till nearly neutralised, and the solution saturated with sulphuretted hydrogen. The precipitate is dissolved in dilute hydrochloric acid and the solution evaporated with sulphuric acid and cautiously ignited. The residue is cadmium sulphate ($CdSO_4$).

L. Marino[1] has described a method for the volumetric estimation of selenious acid by means of permanganate.

Fastness to Light. The cadmium reds appear to be quite as permanent in the light as the technically pure cadmium yellows. Water and oil colour washes underwent no change during a period of two years.

Behaviour in Mixtures (Fastness to Zinc White). Cadmium reds, like the cadmium yellows, are incompatible with the arsenic greens. Two per cent. mixtures with zinc white in the form of water-colour washes, under glass, faded very distinctly in a month.

Chrome Red

This colour, the most basic lead chromate ($Pb_2(OH)_2CrO_4$), is prepared on the manufacturing scale by adding a "cream" of white lead ground in water to a boiling solution of neutral potassium chromate, boiling the mixture vigorously for eight or ten minutes, until it attains a deep violet shade, allowing the resulting precipitate to settle, and

[1] *Z. anorg. Chem.*, 1909, **23**, 143; *J. Soc. Chem. Ind.*, 1909, **29**, 85.

washing it with boiling water. The product so obtained is dull in shade, and must be further treated with dilute sulphuric acid to convert it into true chrome red, after which it is washed to remove the acid. Another process, by which bright shades may be obtained, consists in adding a mixture of basic lead chloride and caustic soda to a boiling solution of potassium chromate, and washing the precipitate formed; subsequent treatment with sulphuric acid is unnecessary. Dark shades cannot be produced in this way.

The great disadvantage in this pigment is its gritty crystalline form. When ground fine the colour is no longer dark red but more or less orange-yellow.

Chrome red finds its chief application as a substitute for vermilion in fresco painting. It can be mixed with oil, but separates again very quickly on account of its high specific gravity. It has the limited fastness of all lead colours.

By suitably influencing the formation (size) of the crystals, very beautiful shades may be obtained, such as those sold under the names of "chrome garnet" and "chrome carmine." Other names applied to it commercially are "Persian red," "Derby red," "Vienna red," "Victoria red," "American vermilion," etc.

Chrome red dissolves in dilute nitric acid to a clear red solution, by which means it may be distinguished from red lead and vermilion. Treated with hydrochloric acid a green solution is formed containing a white precipitate of lead chloride.[1] Analyses are given on p. 488.

VI. Blue Pigments.

The naturally occurring blue pigments, *Lapis lazuli* or native ultramarine, *Azurite* and the *Blue earths* (Vivianite, Ferrous phosphate), are seldom used.

The artificial blue mineral pigments in present use include the *Iron Cyanide Pigments:* Paris blues (Berlin blue), Turnbull's blue; the *Copper* and *Cobalt blues;* and the *Blue Ultramarines.*

Prussian Blues.

(Chinese Blue; Berlin Blue; Paris Blue. Other designations are occasionally used, such as Steel or Milori, Antwerp, Mineral blue, Brunswick blue, etc.)

The typical Prussian blue and the Berlin and Paris blues of commerce are still usually defined as identical substances. E. J. Parry and J. H. Coste[2] have pointed out that the pigments found on the

[1] *Cf.* Zerr and Rübencamp, *Colour Manufacture*, p. 273. [2] *The Chemistry of Pigments.*

market under the names "Prussian blue," "Berlin blue," "Paris blue," "Chinese blue," "Steel blue," "Milori blue," etc., are mixtures of ferric and ferric-potassium ferrocyanides, whereas the blue obtained from potassium ferrocyanide by the action of an excess of ferric salt in acid solution is ferric ferrocyanide free from potassium, and does not occur in commerce. The trade name "Prussian blue" is therefore a collective name. In fact these pigments differ considerably in chemical composition, hue, and stability. Chinese blue is the best quality of Prussian blue and has the average composition shown on p. 514. Brunswick blue is a Prussian blue lake produced by striking the blue on a base of barytes; it may also contain ultramarine. It has replaced Antwerp blue.

According to L. Pelet-Jolivet,[1] the most important technically pure commercial varieties of iron cyanide colours contain the following amounts of potassium and water:—

	Potassium. Per cent.	Water retained at 110°.
Steel blue	21·0	10·5 to 14·0
Steel blue with coppery lustre	19·1	26·7
Prussian blue, ordinary	16·8	29·4 to 37·8
Prussian blue with coppery lustre	15·4	33·6
Prussian blue, dark	12·25	42·0
Prussian blue (theoretical)	0·0	28·0 to 42·0

According to C. Chérix,[2] Steel blue has the composition $K_6Fe''_3Fe'''_4,Fe''_6(CN)_{36}$; and the insoluble Prussian blues the composition $K_4Fe'''_4Fe''_2$, $Fe''_5(CN)_{30}$, with varying amounts of adsorbed water. (*Cf.* Turnbull's blue.) Since all the commercial varieties of Prussian blue described as insoluble in water are not quite insoluble, soluble Prussian blue, $Fe_5(CN)_{12}K_2$, must also be taken into account as a component part of these products. P. Woringer[3] has advanced the view that Prussian blue is a ferrous ferricyanide. T. H. Bowles and J. F. Hirst[4] favour the ferric ferrocyanide formula for the pigment, regard the determination of the iron-cyanogen complex as the best method of valuation, and point to the influence of the alkali present on the combined water content.

Preparation. According to Zerr and Rübencamp,[5] the "direct process" of manufacturing iron cyanide pigments by precipitation of potassium ferrocyanide with excess of ferric salt solution is now only

[1] L. Pelet-Jolivet, *Theorie des Färbeprozesses*, p. 219.
[2] *Etude sur les Bleus de Prusse industrielles*, Dissertation, Lausanne, 1908.
[3] *J. prakt. Chem.*, 1914, **84**, 51; *J. Soc. Chem. Ind.*, 1914, **33**, 148.
[4] *J. Oil and Col. Chem. Assoc.*, 1926, **9**, 153.
[5] *Colour Manufacture*, p. 165.

used for the preparation of a few varieties of Prussian blue, since the pigments obtained by this method cannot compare in beauty of shade with those prepared by the "indirect process."

Chinese Blues, *Steel Blues*, and *Milori Blues* are manufactured almost exclusively by the indirect process, in which Berlin white (white paste), $FeK_2Fe(CN)_6$, is first prepared by the action of potassium ferrocyanide on ferrous sulphate. The product is then converted into the blue by various processes of oxidation. Formerly the oxidation was chiefly carried out by blowing in air. At the present time nitric acid, aqua regia, ferric salts, and, more frequently, chlorine derived from bleaching powder or potassium chlorate and hydrochloric acid are used. Blues made according to a formula where the white precipitate is not treated with acid previous to oxidation are known as Chinese blues; those made where treatment precedes oxidation are known as bronze blues.[1] The process of formation of these blue pigments is still generally regarded as being represented by the following equations:—

$$\text{I. } K_4Fe(CN)_6 + 2FeSO_4 = Fe_2 . Fe(CN)_6 + 2K_2SO_4.$$
$$\text{II. } 3[Fe_2Fe(CN)_6] + 3O = [Fe(CN)_6]_3 . Fe_4 + Fe_2O_3.$$

As an expression of the formation of the Prussian blues these equations are inadequate if the hypothesis be admitted that the potassium-content is not due exclusively to adsorption, but is, in part, a component of the molecule, as must be concluded from the composition of Berlin white.

Composition.	Chinese Blues (Holley).	Prussian Blues (Parry and Coste).[2]
Moisture lost at 100° C.	2·04 to 3·45	3·5 to 5·6
Water of combination	8·75 ,, 18·12	6·2 ,, 18·2
Cyanogen	36·5 ,, 46·1	37·7 ,, 43·0
Iron	32·3 ,, 35·8	29·5 ,, 34·3
Alkali metal—Na	1·6 ,, 3·8	7·6
or K	4·9	2·2 to 7·7
Alkaline sulphate	1·5 to 3·6	...
Silica	0·1 ,, 1·0	...

Although Prussian blues were formerly produced nearly exclusively from potassium ferrocyanide or ferricyanide, the difficulty of obtaining potash during the War led to the preparation of these blue pigments from the iron-cyanogen compounds of sodium. Since a small but definite proportion of adsorbed alkali forms an integral part of Prussian blues, the substitution of sodium for potassium gave a blue inferior in beauty of tone.[3]

[1] E. F. Morris, *J. Oil and Col. Chem. Assoc.*, 1920, 3, 154.
[2] *Analyst*, 1896, 21, 227. [3] S. F. Grove, *Drugs, Oils, and Paints*, April 1919.

Soluble Prussian Blue was formerly obtained by treating a solution of potassium ferrocyanide in excess with ferric chloride. In the preparation on a technical scale sodium sulphate is added to the solutions of the reacting substances, whereby the colour is salted out. The precipitate is washed with water until the washing water begins to turn blue. Another method depends on the solubility of insoluble Prussian blue in oxalic acid. The initial precipitate is ground in the form of paste with crystallised oxalic acid in a mill, and, after some time, the mixture is dissolved in hot water. This pigment was formerly used for colouring paper and also in the dyeing of textiles. It could not be used in painting as it would stain the paper.

Physical Properties of the Commercial Varieties of Iron Cyanide Pigments. The varieties designated "Prussian blues" come into the market in deep blue oblong pieces which are very hard, dense, and tough, and exhibit a strong copper-like lustre both externally and on freshly broken surfaces. This lustre is said to be produced chiefly by the method used in drying (at first slowly at the ordinary temperature, then at 75°-90°). It appears, however, that pressure is also employed. According to Zerr and Rübencamp, these varieties are mostly prepared by the direct process.

The pigments known as "Steel blue" (a special pale bronze blue) or "Milori blue," on the other hand, form dull rectangular pieces, very much lighter in colour than Prussian blue. The Steel blues are lighter than the Milori blues; both brands are of low density, fragile and friable. When ground, they assume only a very imperfect copper-like lustre. So far as is known, these varieties are manufactured exclusively by the indirect process. Intermediate between Prussian blues and Steel blues lie the "Bronze blues." One essential for producing a good bronze blue on a large scale is that the colour should be finely ground. Distinct differences in shade exist between the individual technical products. Besides the typical green-tinged blues other varieties occur possessing a violet tinge and dull shades. The colouring power of the iron cyanide colours is extraordinarily great; no other mineral pigment approaches them in this respect, but they possess less colouring power than most of the blue coal-tar dyes. In addition, they have a pronounced glazing power, a property lost when they are applied in thick coats, on account of their power of absorbing light.

L. Bock[1] considers that the distinction between Paris and Prussian blues is founded upon the purity of the colour, which depends on the quality of the substances used in manufacture. The presence of $FeFe(CN)_5CO$ imparts a violet tinge to the finished blue. The large variety of shades of Prussian blues are due to conditions of temperature and concentration of the solutions, and to the method and extent of

[1] *Z. angew. Chem.*, 1916, **29**, 166.

the oxidation. Steel and milori blues probably differ from Paris and Prussian blues in physical nature and not in higher content of potassium and lower content of iron.

Fastness to Light. The Prussian blues turn white on exposure to light. This action, which is reversible, is regarded by Eibner as due to reduction to Berlin white. The bleaching effect can be stopped immediately by treatment with moist chlorine, nitric acid fumes, or other acid oxidising agents, the blue colour being restored. The change is therefore due to a chemical reaction on which water exercises an accelerating effect. As water colours and in the unmixed state the Prussian blues occupy an intermediate position as regards fastness to light, under normal conditions of moisture. Church found that a water-colour wash in dry air retained its full intensity during a period of four years. On the other hand, when enclosed in a glass tube with ordinary air, it diminished, within thirteen months, from the intensity 10, as measured by Lovibond's tintometer, to intensity 1, and became sea-green in colour. He also observed that soluble Prussian blues were more unstable in the light than the insoluble varieties. An oil-colour wash, on the contrary, became somewhat green after five years and lost only one-tenth of its original intensity. A. Eibner observed no diminution in intensity of Prussian blue artists' colours when kept under glass for two and a half years. Out of nineteen different commercial varieties of Prussian blue only one showed slight diminution in intensity of shade within eight months.

Sensitiveness to Zinc White. The last-named varieties behaved quite differently when made up into pale mixtures with zinc white, and tested in the form of a wash with gum arabic. A. Eibner found that no coloured pigment is altered so rapidly in the light by zinc white as the Prussian blues; 0·5, 2, 4, 8, 16, 32, and 64 per cent. mixtures of all known commercial brands of Prussian blue, Steel blue, Milori blue, etc., faded under glass in direct sunlight (August) within two hours to about half their original intensity, and, at the same time, turned very green. The restoration of the colour in the dark depends on the intensity of the tint and the duration of exposure to the light. The paler mixtures require four months to return to their original intensity of shade, but, for the most part, the green tinge persists. Like other pigments, mixtures of Prussian blues with white lead, heavy spar, lithopone, or whiting suffer less, under the same conditions, than mixtures with zinc white. These diluents protect the blues much less than other coloured pigments.

In oil, the destructive action of zinc white on Prussian blues is very much less than when vehicles soluble in water are employed.

Compatibility in Mixtures. Fastness to Oil. It has long been known that mixtures of Prussian blues and caput mortuum or

vermilion in oil darken after a time. This is probably due, in the first place, not to chemical changes, but to separation of the mixture according to the specific gravity of the pigments. Washes of equal shade made from mixtures of Prussian blue and vermilion, in linseed oil and oil lacquer varnish respectively, behaved differently in that only the former darkened on drying, as the vermilion then had time to separate from the Prussian blue in conformity with its specific gravity. It has been observed that slight double decomposition may take place between Prussian blues and pale cadmium yellows, with the formation of thiocyanates or of potassium ferrocyanide. The former was the product from a cadmium yellow containing oxalate, and the latter with one containing cadmium carbonate.

Fastness to Lime. All the iron cyanide colours are almost instantly decomposed by alkalis, the typical Prussian blues forming ferric hydroxide and potassium ferrocyanide. This reaction serves for the qualitative detection of these pigments. Slaked lime behaves in the same way, but reacts more slowly. Hence the Prussian blues and all mixed colours such as chrome greens and zinc greens cannot be employed in lime or fresco painting. The decomposition by potassium hydroxide is represented by the equation :—

$$Fe_4[Fe(CN)_6]_3 + 12KOH = 3K_4Fe(CN)_6 + 4Fe(OH)_3.$$

Adulterated Varieties are those brands, sold under the names "*Brunswick blue*," "*Berlin blue*," "*Mineral blue*," "*Paris blue*," and the older names "*Hamburg*," "*New*," "*Erlangen blue*." They contain additions of clay, heavy spar, zinc white, magnesia, gypsum, etc. The object of these additions is partly to lower the price, and partly to heighten the shade or produce covering power, as, for example, in Mineral blue. These pigments, in the form of water colours, distempers, etc., are not so fast to light as the untreated Prussian blues.

Antwerp Blue is a mixture of iron and zinc ferrocyanides. It has a violet shade and is duller and covers better than Prussian blue. *Washing Blue* consists of Prussian blue mixed with starch meal.

Analysis. (1) *Technically pure Prussian Blues.* Since commercial Prussian blues, almost without exception, contain potassium, the estimation of the latter is of importance. E. J. Parry and J. H. Coste[1] incinerate the pigment, dissolve the weighed ash in hydrochloric acid, filter off any insoluble matter, precipitate the iron and alumina with ammonia, and after weighing the mixed oxides reduce the iron with stannous chloride and determine it with permanganate ; the aluminium is estimated by difference. After driving off ammonium salts the alkali (in combination as chloride) is determined in the filtrate by

[1] *Analyst*, 1896, **21**, 225.

titration with silver nitrate. The sulphuric acid is estimated in a separate portion of the filtrate. From the figures thus obtained—the weights of alkali salts, hydrochloric and sulphuric acids—Parry and Coste were able to establish the fact that the alkali metal was practically always present either as potassium or as sodium, and never as a mixture of the two metals.

S. F. Grove[1] records an attempt to produce from sodium ferrocyanide Prussian blues equal to those made from the potash salt, by precipitating in the presence of potassium and ammonium salts and thereby effecting a considerable economy of potash salt.

Another weighed amount of the pigment is boiled for some time with potassium carbonate, and the ferric hydroxide obtained dried, ignited, and weighed. The resulting weight multiplied by 0·7 gives the iron other than that present in the radicle. Small amounts of aluminium (1-3 per cent.) were found by Parry and Coste in most of the Prussian blues; this, they state, is not an adulteration, as alum is frequently added as a precipitant in the preparation of these pigments. Potassium ferrocyanide was sometimes present, and could be washed out. According to B. Dyer,[2] the nitrogen is estimated by the method of Kjeldahl. The sulphuric acid should not become blackened during the determination; if coloration takes place, then according to Parry, foreign organic matter is present.

The determination of moisture is carried out at 100°. According to Williamson, the total water-content is best determined by combustion with lead chromate. Parry and Coste state that a pure Prussian blue should contain about 20 per cent. of nitrogen and 30 per cent. of iron, calculated on the dry substance. A "dry" blue should contain under 7 per cent. of water.

Church carries out the qualitative examination for alkali by incinerating the pigment and testing the aqueous extract with turmeric paper. If a Prussian blue contains potassium ferrocyanide, the potassium from the latter will also be present in the ash as potassium cyanide. Church then recommends extraction with hot dilute hydrochloric acid, whereby the potassium ferrocyanide is dissolved. According to Zerr and Rübencamp, the Milori blues often contain tin compounds. (*Cf.* Turnbull's blue.)

The following method is recommended by Fox and Bowles[3]:—*Total Iron and Aluminium.* One g. of the pigment is weighed into a porcelain crucible and gently ignited until the blue colour has completely disappeared and incandescence has ceased. The ash, when cool, is moistened with a few drops of nitric acid, taking care to prevent loss through effervescence, and the excess of acid is evaporated off.

[1] *Drugs, Oils, and Paints*, April, 1919.
[2] *J. Chem. Soc.*, 1895, **67**, 811.
[3] *The Analysis of Pigments, Paints, and Varnishes*, p. 67.

The contents of the crucible are washed into a small beaker with a little distilled water and the crucible is treated with a little hot hydrochloric acid to dissolve any iron compound adhering to the surface, and this, with a little more hydrochloric acid is added to the beaker. The liquid is boiled, diluted, and filtered from any insoluble matter. Ammonium chloride and ammonia are added to the filtrate and the precipitated iron and aluminium hydroxides collected on a filter and well washed. The precipitate is dissolved in hydrochloric acid and the liquid is diluted to a definite volume. The iron is then determined in an aliquot portion by titration with titanous chloride solution [1] or as described under iron oxide pigments (p. 495). In a second portion the combined weight of iron and aluminium hydroxides is obtained gravimetrically and aluminium is thus found by difference. For more accurate work a direct determination of aluminium may be obtained by precipitation with sodium thiosulphate, or by dissolving the combined iron and aluminium hydroxides in dilute hydrochloric acid and adding 1 g. of tartaric acid followed by ammonia until alkaline. The iron is removed by precipitating as sulphide and the clear filtrate is evaporated to dryness. The tartaric acid is then destroyed either by gentle ignition followed by the extraction of alumina with hydrochloric acid, or by evaporating to small bulk with nitric acid when the alumina is precipitated with ammonia and weighed in the usual manner. The iron may similarly be obtained by a direct gravimetric determination by transferring the sulphide to a crucible and igniting to oxide.

Lime. To the filtrate from the iron and aluminium hydroxides one or two drops of ammonium oxalate are added. If calcium is present, a slight excess of the reagent is introduced and the calcium oxalate is filtered off and weighed as CaO in the usual manner.

Alkali Metals. After precipitating any zinc present in the main filtrate as sulphide, a preliminary treatment may be necessary to remove any alkali sulphate initially present as an impurity as, if present, it will interfere with the separation of sodium and potassium by the platinic chloride or perchlorate method. This is accomplished by evaporating to dryness, expelling any ammonium salts and taking up the residue with a few drops of hydrochloric acid and hot water. The sulphate present is then precipitated hot with a minimum quantity of barium chloride and filtered. Excess barium is removed by precipitation with ammonium carbonate and the filtrate evaporated to dryness and the ammonium salts driven off by gentle ignition. The residue is treated with a little hydrochloric acid, dissolved in a few c.c. of distilled water, transferred to a platinum dish, again evaporated to dryness and gently ignited over an Argand burner. This gives the

[1] Fox and Bowles, *loc. cit.*, p. 50.

total potassium and sodium chlorides. The residue is again dissolved in a few c.c. of hydrochloric acid and the potassium determined either as potassium platinichloride or as potassium perchlorate (*cf.* pp. 399-407).

Cyanogen. In the absence of ammonia as a constituent of the pigment, cyanogen may be determined as follows: 0·3 g. of the pigment is weighed into a small specimen tube of such a size that it may be slipped down the neck of a Kjeldahl digestion flask. This is placed in the digestion flask together with 10 g. of sodium sulphate and 20 c.c. of pure concentrated sulphuric acid. A blank determination is similarly made, using the same quantity of reagents, together with a crystal or two of pure cane sugar. One or two drops of a solution of ferric chloride, or a crystal of copper sulphate are added to accelerate the decomposition. The digestion is carried out in a fume cupboard which is free from ammonia fumes. When the acid is colourless or only slightly coloured the flasks are allowed to cool. The contents are rinsed into a distillation flask, about 100 c.c. of concentrated soda solution (sp. gr. 1·3) added until distinctly alkaline, and the liquid steam distilled, the distillate being received in an Erlenmeyer flask containing 100 c.c. of standard $N/10$ sulphuric acid, the end of the adaptor attached to the condenser dipping just beneath the surface of the acid. The Erlenmeyer flask is fitted with a thistle funnel outlet containing a little glass wool moistened with the standard acid. When distillation is complete (in about thirty to forty minutes), the thistle funnel is washed through into the receiver with distilled water and the excess of acid is determined by titration with $N/10$ soda, using methyl orange as indicator. Fox and Bowles prefer adding 10 c.c. of 20 per cent. KI solution and 5 c.c. of saturated KIO_3 solution to the distillate and titrating the liberated iodine with $N/10$ thiosulphate solution, starch, if desired, being used as indicator. The blank is distilled in the same way. One c.c. of $N/10$ H_2SO_4 = 0·0026 g. of cyanogen.

Ammonia. The proportion of ammonia in ammonia Prussian blues may be determined by distilling 1 g. with soda, the distillate being received in 50 c.c. of $N/10$ H_2SO_4. The excess of acid is titrated in the manner indicated in the method for cyanogen above.

Water. (a) *Hygroscopic.* One or two g. of the pigment is heated in a shallow weighing bottle, provided with a close-fitting lid, for two to four hours in a water oven until constant in weight. As the dried pigment is very hygroscopic, care should be taken to keep the weighing vessel well closed during weighing.

(b) *Combined Water.* Short of utilising a full combustion process, combined water is most readily obtained by difference when a complete analysis has been made.

(2) *Adulterated Prussian Blues.* For the detection of adulterants the action of alkalis on the ferrocyanides is employed either by filtering off the ferric hydroxide obtained, dissolving it in sulphuric acid, and titrating the reduced solution with permanganate; or by determining the potassium ferrocyanide formed, by one of the standard methods. (*Cf.* Vol. I., pp. 630-638.) The quantity of pigment found is compared with the quantity contained in a technically pure Prussian blue.

Another method of determination is that of M. Dittrich and C. Hassel,[1] which is carried out as follows:—The blue is decomposed into ferric hydroxide and sodium ferrocyanide by boiling with pure sodium hydroxide. When the reaction is complete the ferric hydroxide is filtered off, well washed, the filtrate treated with 37-40 c.c. of 10 per cent. ammonium persulphate solution, acidified with dilute sulphuric acid, and heated until all the sodium ferrocyanide is decomposed. The two iron precipitates must be dissolved again and reprecipitated, as a large quantity of alkali adheres to them.

A sample of Brunswick Blue analysed by Hurst gave the following numbers:—

H_2O	0·28
Al_2O_3	2·45
Fe_2O_3	3·31
Barytes and silica	89·86
Cyanogen and sulphur	4·10
	100·00

The qualitative determination of the mineral admixtures is carried out according to the method of Bolley-Stahlschmidt,[2] by first decomposing the cyanogen compounds. Two g. of the Blue is mixed with an equal weight of ammonium nitrate and three times the weight of ammonium sulphate, and the mixture heated in a small tubular retort provided with a receiver but not luted to it. All basic compounds, with the exception of ammonia, remain in the retort. The residue is warmed with water slightly acidified with hydrochloric acid, in which heavy spar, gypsum, clay, and sand remain undissolved, and the separate constituents of the hydrochloric acid solution and of the insoluble residue are identified by the usual tests.

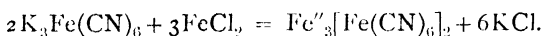
Another method is to boil the blue with ammonia until it is entirely decomposed, and then filter. The filtrate will contain zinc and magnesia if present, also ammonium ferrocyanide. The zinc and magnesia are recognised by the usual tests, and the ferrocyanide by making a portion of the solution slightly acid with hydrochloric acid and

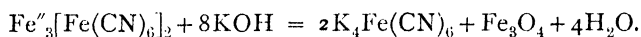
[1] *Ber.*, 1903, **36**, 1932. Also, C. Coffignier, "Verfahren zur Bestimmung von Berliner Blau," *Bull. Soc. Chim.* [3], 1904, **31**, 391; *J. Soc. Chem. Ind.*, 1904, **23**, 456.

[2] *Handbuch der tech. chem. Untersuchungen*, 6th ed., p. 298.

adding a solution of ferric chloride or ferrous sulphate. Theoretically it is the ferric salt that should be added, but in practice the ferrous salt has often to be used. The blue colour of Prussian blue reappears. The brown residue (after the original boiling with ammonia) is filtered off, washed well and dissolved in hydrochloric acid. A white residue would indicate the presence of barium sulphate, china clay, etc., and special tests for its identification should be applied, while the solution will contain the iron, alumina and calcium, if present.

Turnbull's Blue (insoluble) is formed by the action of a ferrous salt in excess on potassium ferricyanide. It was first prepared by Gmelin, and was then considered to be ferrous ferricyanide formed according to the equation:—

$$2K_3Fe(CN)_6 + 3FeCl_2 = Fe''_3[Fe(CN)_6]_2 + 6KCl.$$

On warming it with alkalis, however, potassium ferricyanide is not regenerated, only potassium ferrocyanide and a mixture of hydrated ferric and ferroso-ferric oxides being formed. This reaction was formerly expressed by the equation:—

$$Fe''_3[Fe(CN)_6]_2 + 8KOH = 2K_4Fe(CN)_6 + Fe_3O_4 + 4H_2O.$$

K. A. Hofmann[1] is of opinion that an interchange in the state of oxidation of the iron takes place in this decomposition. E. Müller and T. Stanich[2] found that freshly prepared Turnbull's blue is, in fact, a ferrocyanide, but is not identical with Prussian blue, since ferrous iron is also present apart from the radicle, together with potassium and ferric iron, and as a result of their investigations suggested the formula $KFe''Fe'''_3[Fe''(CN)_3]_3$.

Experiments by A. Eibner, made to gain information as to differences in colour, fastness to light, and miscibility of Prussian and Turnbull's blues, proved that freshly prepared Turnbull's blue which has been rapidly washed is not identical with the typical Prussian blues, either in shade or stability to light and vehicles. It possesses an ugly tone resembling that of indigo, and when made up as a water-colour wash of deep shade fades very markedly within three weeks. This reaction is reversible. The longer it is in contact with air during the process of washing, the more stable to light does it become. The behaviour of Turnbull's blue with zinc white is essentially different from that of Prussian blue, and it is more sensitive towards organic vehicles than the latter.

The soluble modification of Turnbull's blue, when treated with various metallic salts, especially those of tin, forms particularly beautiful insoluble blue compounds. An exceptionally fine Turnbull's blue con-

[1] *Annalen*, 1904, **337**, 1; 1905, **340**, 267; 1905, **342**, 364; *J. Soc. Chem. Ind.*, 1904, **23**, 1209; 1905, **24**, 1221.

[2] *J. prakt. Chem.*, 1909, **79**, 81.

taining tin can also be obtained by mixing together solutions of potassium ferricyanide and a ferric salt, and adding stannous chloride.

The presence of tin in Turnbull's blue may be detected by fusing it with a mixture of sodium carbonate and saltpetre, and dissolving the melt, which contains the tin as sodium stannate, in hydrochloric acid. The solution is filtered, if necessary, and when treated with sulphuretted hydrogen, tin sulphide gradually separates out.

Turnbull's blue cannot be employed as an artists' pigment, on account of its instability and dull shade. Nevertheless, according to Church, it forms a component part of many commercial Prussian, Steel and Milori blues, and is the cause of their instability in the light. The same ideas are expressed in Chérix's formulæ for Prussian and Steel blues (p. 513); it would appear that, in the oxidation of the "white paste," the iron outside the radicle is not completely changed into the ferric state. On the other hand, Eibner, on examining a considerable number of commercial Prussian and Steel blues, found no ferrous iron, whereas the latter was present in all Turnbull's blues, whatever the method of preparation.

Freshly precipitated Turnbull's blue made up as a wash with gum arabic is much less stable than the Prussian blues. Test portions faded within three weeks to about half the original intensity, and became sea-green in colour. In the dark, or under the influence of acid oxidising agents, this reaction is reversed. As in the Prussian blues, the change is therefore brought about by reduction, but in Turnbull's blue the ferric iron portion outside the radicle is affected.

Blue Copper Colours.

These artificial pigments consist essentially of cupric hydroxide, the pale and somewhat greenish shade of which depends on the method of manufacture. They are for the most part durable in lime, hence the name "*Lime blue*"; but they are not applicable as oil colours, since they turn green in oil, forming copper salts of fatty acids. During recent years they have been largely displaced by ultramarine and by the coal-tar colour lakes. They are still used for painting exteriors, in house painting, and in distemper.

Mountain Blue. This name has been transferred from the mineral "azurite" to the artificial product, although the latter does not possess the same composition as the mineral. The colour is prepared from cupric chloride obtained by the action of calcium chloride on copper sulphate; the cupric chloride is treated with lime paste, producing green copper oxychloride, which is then converted into the blue colour by adding potassium carbonate and milk of lime. Its composition corresponds to the formula $2CuCO_3+Cu(OH)_2$.

Lime Blue is prepared in a similar manner, but in one operation, by precipitating a solution of copper sulphate with milk of lime, with addition of ammonium chloride. It consists of cupric hydroxide, mixed with lime. Lime blue sold in the form of oblong rectangular lumps is known as *Neuwied blue.* The name "lime blue" is now generally applied to the lime-fast blue coal-tar colour lakes and to ultramarine cheapened by the addition of gypsum.

Bremen Blue is manufactured by the "direct process" as follows:—Green basic copper sulphate is precipitated by treating a solution of copper sulphate with sodium carbonate solution of sp. gr. 1·075, and the product is converted into the blue by further treatment with a more concentrated solution of sodium carbonate of sp. gr. 1·26. In the "indirect process" a solution of copper sulphate is mixed with common salt, scrap copper, and caustic soda, the mixture placed in oxidation boxes, and left to react in the presence of air for several months, whereby green cuprous oxychloride is formed. The product, after being passed through a sieve to remove unoxidised particles of copper, is treated with a definite quantity of hydrochloric acid, and finally converted into the blue by means of caustic soda at a temperature not exceeding 30° to 35°.

It consists mostly of copper hydroxide $Cu(OH)_2$ with small quantities of carbonate of copper.

Blue Verditer is a pigment of a sky-blue tint, very similar to Bremen blue in its composition and mode of preparation (the percentage of copper sulphate present may vary from 9 to 31).

Gypsum, ground pumice-stone, infusorial earth, etc., occur as adulterants in these copper colours. The analysis is carried out by the usual methods, and includes the estimation of copper and water, and also the amount of additions.

Oil Blue.[1] This pigment, which is a specially prepared form of copper sulphide, is applicable as an oil colour. It is manufactured by introducing copper filings into boiling sulphur; after cooling, the mass is boiled with caustic soda in order to remove the excess of sulphur. This colour is unaffected by sulphuretted hydrogen, but it can be used only in linseed oil varnish, as it becomes oxidised in other vehicles.

Blue Cobalt Colours.

These colours consist essentially of glass fluxes or alumina (cobalt aluminates with alumina) coloured blue by cobalt oxide; hence they approximate to the native substratum pigments (ochres, etc.). For their preparation cobalt salts, or roasted cobalt ores known as "zaffres," are employed.

[1] The name "Oil Blue" is also applied to Prussian blue.

Smalts.

This colour is a cobalt silicate containing potassium, and is obtained by fusing *zaffres*[1] with quartz sand and potassium carbonate in a glass-furnace. The potassium carbonate cannot be replaced by sodium carbonate, as cobalt sodium glasses never give a pure blue colour, but a red or brown shade. Smalts contains about 65-72 per cent. silica, 2-7 per cent. cobaltous oxide, 2-22 per cent. potassium, and about 0·5-20 per cent. alumina. It also contains small quantities of lime, iron, and nickel, and, in most samples, arsenious acid, which was formerly added purposely as it increases the beauty of the colour. Nickel is a particularly harmful impurity of zaffres, as it imparts a violet tinge to the smalts. Bismuth is almost as detrimental, causing the glass to become greenish-blue. Iron in any great quantity is also to be avoided as it produces a dirty appearance in the product.

Smalts, being a kind of glass, has poor covering power, and has been displaced by ultramarine and cobalt blue, practically its only use at the present time being for painting earthenware, and as a blueing and bleaching agent where a permanent effect is required. It differs from cobalt blue in being fusible. Like cobalt blue smalts is insoluble in dilute acids and alkalies, but is decomposed by long digestion with concentrated hydrochloric acid, yielding the chlorides of the metals it contains and a residue of gelatinous silica.

The methods of *Analysis* are as described under "Cobalt Blue" (see also p. 330).

Cobalt Blue.

(Thénard's Blue; Cobalt Ultramarine; Azure Blue.)

Cobalt blue is prepared, according to Leithner, by calcining a mixture of cobalt nitrate and alumina, or by mixing a solution of alum with a solution of a cobaltous salt, treating the mixture with alkalis, and calcining the precipitate obtained. Thénard calcined a mixture of aluminium hydroxide and cobaltous phosphate or arsenate.[2] The presence of phosphoric acid favours the formation of the colour and increases its beauty.

The cobalt blues are generally described as cobalt aluminates, but the commercial brands contain, according to the shade, varying amounts of cobalt (between 19 and 30 per cent.), the highest of which does not reach the theoretical content, viz., 36·6 per cent. for cobalt aluminate. Moreover, the cobalt blues prepared from phosphates are constituted differently from those containing no phosphates, the term aluminates applies approximately only to the dark varieties prepared without

[1] For the better qualities oxide of cobalt is used.

[2] *Dingl. polyt. J.*, 1834, **53**, 447; 1836, **54**, 339; also, A. Munkert, *Die Normalfarben*, p. 113.

phosphoric acid. W. Stein[1] considers the cobalt blues to be molecular mixtures of alumina and cobalt oxide. (*Cf.* Ultramarine.)

Two brands of cobalt blue are usually found in commerce, viz., pale and dark, which differ in the amount of the colouring principle present. The cobalt blues are insoluble in dilute acids and alkalis, and by treatment with these reagents adulteration with ultramarine and copper blues or Prussian blue respectively can be easily detected. They are decomposed by fusion with alkali, also by strongly heating with concentrated sulphuric acid for some time, when a violet solution and a white powder result; this powder dissolves on addition of water, and the resulting clear blue solution can be examined by the ordinary group tests. The covering power is small. Like the blue ultramarines they have a dirty violet appearance in artificial light. In art painting they are employed as oil and water colours for colouring porcelain, and for printing bank-notes in countries where a blue is used for this purpose, as the colour cannot be reproduced by photographic processes.

They are perfectly fast to both air and light. When made up with zinc white as a water colour, however, they fade distinctly within two months.

Analysis. A. Munkert[2] reduces the pigment, when phosphoric and arsenic acids are absent, by heating in a current of hydrogen, dissolves the black mass in hydrochloric acid, and separates the cobalt from the alumina by means of sodium acetate. If the acids mentioned are present, the pigment is fused with six times its weight of potassium carbonate, the melt extracted with water, the solution filtered off, and the insoluble residue subjected to further fusion with potassium carbonate until it is completely decomposed, when it is again extracted with water and filtered. The decomposition can be effected in a single operation by fusing with ten times the weight of alkali hydroxide in a silver crucible. The combined filtrates are acidified with nitric acid, and evaporated to dryness. After taking up the residue with water, the aluminium is precipitated by ammonium hydroxide together with phosphoric and arsenic acids and silica. Silica is separated by dissolving the precipitate in nitric acid, evaporating down the solution, extracting with water, and filtering. The filtrate is evaporated down with sulphuric acid to remove the nitric acid, and is then treated repeatedly with ammonium sulphate and alcohol, whereby the aluminium is separated out as aluminium ammonium sulphate. The precipitate is washed with alcohol, ignited, and the aluminium estimated as Al_2O_3. After evaporating off the alcohol, arsenic is precipitated as the sulphide in the combined filtrates, and after filtration, the phosphoric acid precipitated with ammonium molybdate.

[1] *Dingl. polyt. J.*, 1871, **201**, 420.
[2] *Normalfarben*, p. 116.

The black residue obtained after fusion consists of crystalline spangles of cobaltous oxide. If the estimation of the very small traces of nickel, iron, and copper contained in the residue has not to be carried out, the latter, after thorough washing, may be reduced directly according to Rose's method, ignited a second time in the current of hydrogen, washed in order to remove alkali, and weighed as metallic cobalt.

Cœruleum.

(Cerulean Blue; Bleu Céleste.)

This colour is manufactured by calcining a mixture of cobaltous sulphate, tin salt, and chalk, the tin thus taking the place of alumina in the cobalt blues. Cœruleum has a more greenish tinge than the latter; hence its shade remains unchanged in artificial light. Its average composition is 50 per cent. stannic oxide, 18 per cent. cobaltous oxide, and 32 per cent. gypsum. It covers better than the cobalt blues and is used almost exclusively as an artists' colour.

Green-blue Oxide is an artists' pigment which has recently come on to the market. It is manufactured by calcining a mixture of chromic oxide, alumina, and cobalt salt. It covers better than cobalt blue.

Manganese Blue is produced, according to Bony,[1] by a process of calcination very similar to that used in the manufacture of ultramarine. A mixture of China clay, oxides of manganese, and barium nitrate, approximately in the proportion 2 : 3 : 8, is heated to redness in an oxidising atmosphere; compounds of iron must be excluded. The pigment is obtained in several shades varying from violet to sky-blue, but up to the present it has found little application.

The ancient cœruleum or Egyptian blue was originally prepared by putting together a mixture of copper ore, sand, and sodium carbonate, a bright pale blue being thus obtained consisting essentially of silicates of copper and sodium. L. Bock[2] assigns to it the formula CaO, CuO, $4SiO_2$.

Ultramarine.[3]

(Lapis Lazuli Blue (for Native Ultramarines); Oriental Blue.)

The ultramarines differ from all other inorganic pigments as they cannot be valued by chemical analysis, the colouring principle not being present in a form which can be dealt with by analytical methods. The quantitative estimation of individual constituents in the different commercial brands of blue and other coloured ultramarines does not indicate the quality of products similar to one another in shade; and

[1] *Farben-Zeit.*, 1907, **13**, 77. [2] *Kolloid Z.*, 1917, **20**, 145.

[3] *Cf.* R. Hoffmann, *Ultramarin*, 1902. Knapp and Ebell, *Dingl. polyt. J.*, 1878, **229**, 69, 173. Heumann, *Annalen*, 1871, **199**, 253; 1872, **201**, 262; 1872, **203**, 174.

apart from the identification of foreign admixtures, is less important than practical tests of the stability and compatibility of the products in mixtures with other pigments. The material and technical identity of artificial blue ultramarines with native lapis lazuli cannot be discussed while the composition of the two substances is incompletely explained. Many theories of the cause of the colour of ultramarine have been propounded; the older views are quite untenable. K. A. Hofmann and W. Metzener[1] have advanced the view that the blue sulphur sesquioxide of R. Weber[2] bears a relation to the chromophore of the blue ultramarines. It has since been assumed that particular physical condition of the sulphur is the cause of the colour exhibited by the blue ultramarines. Lately, it has been thought that the solution of the problem is to be found in the assumption that the sulphur is dissolved or adsorbed, and in this condition is able, like iodine, to assume different colours according to the nature of the receptive medium.[3]

The occurrence of the purple-red selenium and the green tellurium ultramarines of Guimet,[4] of the organic ultramarines of de Forcraud[5] and of the older silver ultramarines, shows that the blue ultramarines contain components which can undergo substitution. Rohland,[6] by heating talcs with sodium carbonate and sulphur, obtained green compounds which behaved like ultramarine, but in which the coloured component could be extracted with water. Notelle and Corblet[7] observed that the silica used in the preparation of ultramarine plays only a mechanical part, and, on attempting to replace it by other substances, they succeeded in obtaining a larger yield of pigment of considerable strength of colour. F. Singer has prepared green to greenish-blue pigments of the nature of ultramarine by heating or fusing zeolites with alkali sulphides.[8]

An account of the boron ultramarines, together with a discussion of some views on the nature of the colouring principle in the silica ultramarines, has been published by J. Hoffmann.[9]

The researches on the constitution and the colouring principle of ultramarines, have led to the conclusion that these bodies are not individual coloured substances like, for example, cinnabar, whose colour is mainly dependent on the constant relative proportions by weight of its components, but that they contain a still unknown colour principle which is firmly held by a non-coloured basis, somewhat in the same way as the coloured components in the organic colour lakes. Whether it is

[1] *Ber.*, 1905, **38**, 2482; *J. Soc. Chem. Ind.*, 1905, **24**, 898.
[2] *Pogg. Ann.*, 1875, **156**, 531.
[3] R. Rohland, "Ueber das Farbproblem des Ultramarins," *Phys. Chem. Zentr.*, 1908, p. 514.
[4] *Bull. Soc. Chim.*, 1902, **27**, 480; Morell, *ibid.*, 1902, **28**, 522.
[5] *Comptes rend.*, 1879, **88**, 30.
[6] *Loc. cit.*
[7] *Farben-Zeit.*, 1909, **15**, 1199.
[8] Ger. Pat. 221344 of the 17th July 1909.
[9] *Chem. Zeit.*, 1910, **34**, 821; *J. Soc. Chem. Ind.*, 1910, **29**, 1066; *Kolloid Z.*, 1912, **10**, 275.

a question of chemical combination or of adsorption is still unsolved. From the researches made up to the present, it follows that the technically pure unadulterated ultramarines must, without doubt, be looked upon not as "primitive pigments" but as "substratum pigments." The adulterated qualities are produced by the addition of gypsum, chalk, etc., as diluents.

L. Bock[1] concludes that the grouping Na, Al, SiO_2, in the ultramarine molecule is similar to that in zeolites, because of its formation from them by treatment with alkali sulphides. A good summary of the theories regarding the composition of ultramarines has been given by J. S. Remington.[2] Their relationship to natural and artificial silicates is stated as follows:—zeolite, CaO, $Al_2O_3 . 2SiO_2 . 3H_2O$; lapis lazuli, $3(Na_2O . Al_2O_3 . SiO_2)Na_2S_4$; "sulphur rich," "silica poor," ultra-blue, $3(Na_2O . Al_2O_3 . 2SiO_2)Na_2S_2$; "sulphur poor," "silica poor," ultra-green, $3(Na_2O . Al_2O_3 . 2SiO_2)Na_2S_2$; "silica poor," "sulphur rich," ultra-blue, $2(Na_2O . Al_2O_3 . 3SiO_2)Na_2S_4$.

The state of combination of sulphur in the various products is still doubtful (H. H. Morgan[3] and T. H. Barry[4] have shown that 0·5-1 per cent. S can be extracted by CS_2 or by ether). Remington concludes that ultramarines rich in silica approximate to double silicates, while when rich in alumina they approximate to aluminium silicates, and that sodium is less readily replaced in the double silicates than in aluminium silicates. The existence of isomeric ultramarines containing – SNa or – SONa groups attached to Al or Si respectively is considered probable.

The present-day manufacture and methods of testing are described by R. H. Underwood.[5]

Chemical Analysis. The analytical control of the ultramarine manufacture comprises the analysis of the raw materials, the control of working conditions, and the examination of the finished product[6]

The losses in the manufacture of ultramarine are still great; in the burning process alone they amount to about 40 per cent., so that from the original mass 60 per cent. or at most 65 per cent. of raw product is obtained, and the latter, when washed, loses 20-25 per cent. and even up to 30 per cent. of soluble salts. The yield of finished blue from the original mass, taking an average of many years' experience, amounts to 48-50 per cent.

There is no doubt that these losses will be reduced, on chemical or on technical lines, and a higher yield obtained. A wide field is here open for investigation; in addition, means for utilising the escaping sulphuric and sulphurous acid gases are to be desired.

[1] *Z. angew. Chem.*, 1915, **28**, 147; *Farben-Zeit.*, 1920, **25**, 761. [2] *Industrial Chemist*, 1926, **2**, 79.
[3] *J. Oil and Col. Chem. Assoc.*, 1919, **2**, 120. [4] *Ibid.*, 1925, **8**, 202.
[5] *Drugs, Oils and Paints*, 1924, **40**, 301.
[6] Rawlins, *J. Soc. Chem. Ind.*, 1887, 791. R. Hoffmann, *Ultramarin*, 1902.

ANALYSIS OF ULTRAMARINE.

Ultramarine can easily be detected by its behaviour towards dilute acids—the blue colour is destroyed, sulphuretted hydrogen is evolved and sulphur deposited. It is not acted upon by alkalis, nor is it affected by heat.

Admixture with barytes, gypsum, whiting, etc., can be recognised by the flame test. Quantitatively, along with the silica and alumina of the ultramarine, they are determined as follows: About 2 g. of the sample is heated with hydrochloric acid until the colour is entirely destroyed; the mixture is evaporated to dryness and gently ignited, heated again with hydrochloric acid, diluted, and the silica and barium sulphate (if present) filtered off, washed, etc., and a portion fused with fusion mixture for the estimation of the barytes. To the filtrate ammonium hydroxide is added in slight excess; alumina is precipitated, filtered off, washed, etc. To the filtrate from this precipitation ammonium carbonate is added to precipitate any calcium present.

The works' analysis of ultramarine is confined to the estimation of free and chemically combined silica, alumina, sodium (Na_2O), and total and free sulphur. The quality or intensity of the colour may be arrived at by comparing the sample with a standard ultramarine by viewing them, after being pressed out by a spatula on a piece of white paper or white glazed tile. When it is desired to measure the intensity of the colour, 1 g. of standard ultramarine is mixed in a mortar with known quantities of kaolin and the samples compared in a north light. To test ultramarine for resistance to alum, 0·1 g. is shaken with 10 c.c. of a 10 per cent. solution, and the tone after standing noted.

1. Preparation of the raw Ultramarine for Analysis.—The colour is finely powdered and passed through a silk gauze sieve, after which it is dried at 100° for about twenty-four hours. From 2-10 g. is then weighed out and extracted with water, the solution made up to 500 c.c., filtered, and 100 c.c. taken for each of the following determinations:—

1. $Na_2S_2O_3$. By titration with iodine solution and starch; the result is expressed as $Na_2S_2O_3$.
2. Na_2SO_4. By precipitation with barium chloride in acid solution.
3. NaCl. By precipitation with silver nitrate. (Sodium chloride is very seldom present in raw ultramarine.)

If it is desired to determine the glucose in a sample, this can be done by lixiviating a weighed quantity of the blue in water, making up to a standard quantity and determining the glucose with Fehling's solution.

From 10-20 g. of ultramarine is partially washed by decantation two or three times successively, a quantity of alcohol being added in

order to ensure a clear filtrate. The residue is treated with a dilute solution of sodium sulphite and the mixture evaporated nearly to dryness on the water-bath; this is done in order to remove free sulphur, as carbon disulphide will extract only 40-60 per cent. of the latter. The residue is then washed until a dried portion of the ultramarine, when moistened with a little water and filtered, gives no trace of turbidity with barium chloride in the filtrate. This last operation is very important, as otherwise the drying at a later stage cannot be effected without change in the composition of the ultramarine. If the ultramarine is washed completely free from soluble salts, the blue, red, and yellow varieties may be dried at 100°-140° or even at 150° without the slightest change taking place.

After being again finely powdered and dried at 130°-140°, the ultramarine is transferred, while still hot, to a glass stoppered bottle.

2. **Free Sulphur.** H. H. Morgan (*loc. cit.*) extracts in a Soxhlet with methylated ether for one or two hours. The method is accurate and the amounts vary from 0·18 to 1·55 per cent.

3. **Estimation of Silica, Clay Residue, Total Sulphur, and Sulphur as Sulphuric Acid.**—One g. of the dry substance is weighed into a porcelain dish, agitated as carefully as possible with water, and treated with 1-2 c.c. of bromine. Unless this operation is carried out with extreme care, small lumps are formed which are decomposed only on the outer surface, while inside the ultramarine is scarcely attacked at all. When the bromine is partially dissolved, as shown by the yellow colour of the liquid, 15-20 c.c. of nitric acid is added and the liquid evaporated to dryness on the water-bath. The residue is then taken up with water, about 20 c.c. of hydrochloric acid added, the solution again evaporated, the residue treated with hydrochloric acid, the mixture allowed to stand for some time (in the cold for twelve hours, hot for three hours), diluted with water, and filtered. The silica and clay residue (sand) remain on the filter paper, and are separated from one another as in the analysis of clay. The total sulphur is determined by heating the filtrate to boiling and precipitating with barium chloride. If the amount of iron in the ultramarine is considerable, which seldom occurs, the filtrate from the barium sulphate is reduced with zinc and titrated with permanganate solution.

Another method for estimating the total sulphur is to treat about 2 g. of the ultramarine with a mixture of 2 parts nitric acid and 1 part hydrochloric acid until the colour is completely decomposed and only a transparent mass of silicate is left: the mixture is diluted and filtered and the sulphur (now present as sulphate) in the filtrate precipitated by barium chloride.

Sulphur as sulphuric acid is estimated as follows: 2 g. of ultramarine is treated with dilute hydrochloric acid, the precipitated sulphur and

silica filtered off, and the filtrate precipitated with barium chloride. To find the amount of SO_3 present the weight of $BaSO_4$ is multiplied by 0·34335.

4. **Estimation of Alumina and Sodium Oxide** (Na_2O).—One g. of ultramarine, washed and dried as described above, is, as before, very carefully agitated with water and treated with excess of hydrochloric acid. After standing for some time, with occasional stirring, the mixture is heated until the solution becomes clear on allowing it to settle. The solution is then filtered off, when the sulphur, clay residue, and some silica remain as an insoluble residue; this residue is ignited and weighed. The filtrate is evaporated to dryness, the residue moistened with water and hydrochloric acid, again dried, then treated with hydrochloric acid, and the solution, after standing for a short time, diluted with water and filtered. Silica remains on the filter paper, and, when added to the residue obtained in the first filtration gives the amount of total silica and clay residue, which serves as a useful control of the determination described under (2).

The filtrate is evaporated to dryness to remove the excess of hydrochloric acid, the residue dissolved in water, precipitated with ammonia, and the whole again taken down completely to dryness on the water-bath. The alumina thus obtained can be washed easily and completely. The residue is taken up with hot water, the solution treated with a few drops of ammonia, heated, and filtered; the alumina remaining on the filter paper is ignited and weighed. Sodium (Na_2O) is determined by treating the filtrate with sulphuric acid and fuming nitric acid, and evaporating to dryness; by this treatment the creeping of the salts up the sides of the dish does not take place. The residue is very strongly ignited, and the amount of sodium as Na_2O calculated from the weight of sodium sulphate obtained.

5. **Examination for Additions insoluble in Acid.**—The following method devised by E. R. Andrews[1] facilitates the examination of the pigment for the possible presence of foreign additions insoluble in acid, an operation not easily performed when the sample is analysed by decomposition with acid. The process depends on the oxidising action of bromine and the subsequent complete solution of the products when the pure pigment is thus treated. One g. of the ultramarine is placed in a wide-mouthed flask of 150 c.c. capacity, and thoroughly wetted with 5-10 c.c. of water; about 30 c.c. of an aqueous saturated solution of bromine is then added, and the contents of the flask agitated until the colour of the bromine begins to disappear. More bromine water is added gradually until the blue colour of the ultramarine disappears and an excess of bromine remains. The flask

[1] *Analyst*, 1910, **35**, 157.

is set aside for fifteen minutes, and the contents are then filtered quickly. The residue is washed with water, ignited, and weighed. The filtrate is acidified with 10 c.c. of strong hydrochloric acid, evaporated to dryness, the residue extracted with water, the silica filtered off, and the filtrate made up to a known volume. Aliquot portions of this solution are taken for determining the alumina, sulphur, etc. The weighed residue is boiled with sodium carbonate, filtered, washed, and re-weighed, the loss in weight being due to the invariable presence of a little silica in the insoluble residue. The amount of silica thus found (usually about 1·5 per cent.) is added to the bulk of the silica in the main filtrate. The matter insoluble in bromine water is stated to vary from 2·4-4·4 per cent. and to consist mainly of clay.

Note.—The statement frequently found that sodium sulphide is a constituent of ultramarine, is not to be taken in the sense that this compound is present in the free state, but that its constituents are united with other elements, probably with aluminium, to form a complex product. This assumption explains the insensitiveness of the ultramarines towards white lead and other lead colours.[1] However, L. Bock[2] regards the sulphur compounds in ultramarine as substitutes of water in zeolites, and states that this assumption being correct, it is also quite justifiable to consider that the sulphur in ultramarine must be chemically combined.

Typical Analyses of Ultramarines.

	Ultramarine Blues (Holley).			Ultramarine Blues (Hurst).			Ultramarine Blues (Remington).			Ultramarine Green (Hurst).
	I.	II.	III.	Soap Makers.	Calico Printers.	Paper Makers.	Soap Makers.	Calico Printers.	Paper Makers.	
SiO_2 .	39·26	39·45	41·92	40·65	40·89	45·42	40 62	40·72	46·21	38·52
Al_2O_3	25·60	25·81	26·21	25·05	24·11	21·15	25·17	24·30	21·30	28·94
S .	11·69	12·02	10·82	12·95	13·74	11·62	12·96	13·86	11·70	8·30
SO_3 .	3·10	2·33	1·93	4·81	3·05	5·58	4·92	3·12	5·82	...
Na_2O	19·87	19·73	18·40	14·26	15·61	9·91	14·35	15·7	9·95	23·68
H_2O .	0·48	0·66	0·72	2·28	2·60	6·32	1·98	2·29	4·92	...

Properties of technical Importance in Painting. Blue ultramarines are unstable towards sulphur dioxide. They are frequently looked upon as absolutely fast to light and air, but this does not appear to be invariably correct. Moreover, according to A. W. Keim, they are not all fast to lime. In fresco paintings, lime which is rich in silica destroys them in a comparatively short time, with the formation of

[1] *Cf.* A. Eibner, "Ueber Ultramarine," *Techn. Mitt. f. Malerei*, 1907, **23**, 270.
[2] *Z. angew. Chem.*, 1920, **24**, 23; *J. Soc. Chem. Ind.*, 1920, **39**, 306A.

discolouring or colourless compounds. It is very probable that this change is aided by moisture, which also appears to play some part in the so-called "ultramarine disease." According to Pettenkofer,[1] this "disease" also occurs with the green earths (and with those pigments in general which are rich in clay, and therefore able to condense a large amount of water on their surfaces) in oil paintings subjected to great variations in temperature and moisture. He attributes the "disease" in such oil paintings to the fact that the "disease" of the colour itself, wherever it occurs in the painting, causes the vehicle (oil, etc.) to be more easily affected by moisture and changes of temperature, thus allowing the pigments to be visible through the cloudy medium of the disintegrated oil-layer. Rohland traces the "ultramarine disease" to the superficial decomposition of the pigment by hydrolysis. E. Täuber has called attention to the relative lack of fastness to light of the violet ultramarines.[2]

Behaviour of Ultramarines in Mixtures. It is frequently stated that ultramarines, since they are sulphur colours, must react with lead pigments. These assertions are based partly on correctly made observations but wrong inferences, and also owing to the technical impurity of one of the components, in this case the white lead. A. Eibner obtained the following results:—(1) Pure blue ultramarine, when boiled with a solution of lead acetate, is very strongly discoloured to blackish-blue; on the other hand, when boiled with pure white lead for the same length of time it remains unchanged. The discoloration is therefore caused by the technical impurity (lead acetate) in white lead, as in the vermilion—white lead mixtures. (2) Mixtures of the pure pigments remained unchanged for four years, and mixtures of the colours in oil for five years.[3]

Fastness to Zinc White. A. Eibner found that the blue, as well as the green, violet, and red ultramarines, when made up into pale mixtures with zinc white and exposed in the form of water colours under glass to direct sunlight, faded distinctly within four months.

VII. VIOLET PIGMENTS.

Cobalt Violet.

By mixing solutions of cobalt sulphate and sodium phosphate, a rose-red precipitate of hydrated cobaltous phosphate is formed, which, on fusing, loses water, and assumes a violet colour. The melt is broken up, ground, washed, and dried, and then forms the dark cobalt violet of commerce. This pigment is semi-glazing, and permanent in

[1] *Ueber Oelfarbe*, 1902. [2] *Farben-Zeit.*, 1910, 15, 1382.
[3] *Cf.* A. Eibner, *Malmaterialienkunde*, p. 180.

mixtures with other mineral pigments. It is stated, however, that in practical use as a tempera or water colour it undergoes change of tone owing to gradual absorption of water. It appears to be quite fast to light. Washes prepared with gum arabic and with oil remained completely unchanged for seven years. Cobalt violet is also very stable towards zinc white. Twelve per cent. mixtures in the form of water colours, exposed under glass to light, remained quite unchanged during two months.

A pigment differing from this form of cobalt violet is the cobaltous arsenite prepared by Gentele, which is a delicate red-violet powder, similar in shade and composition to the mineral, "cobalt bloom." It comes on the market under the name "Pale Cobalt violet," and is easily distinguished from the product described above by the odour of arsenic which is given off when it is heated on charcoal. This pigment is also very resistant towards zinc white. Twelve per cent. mixtures in the form of water colours, spread out under glass and exposed to light, showed no change in two months (October to December).

Manganese Violet, Mineral Violet.

According to Mierzinski, this colour is prepared by fusing in enamelled cast-iron vessels a mixture of phosphoric acid and either finely powdered pyrolusite or the residues from the preparation of chlorine. The mass thus obtained is allowed to cool, and is then heated up to boiling with ammonia or ammonium carbonate solution, when manganese dioxide precipitates out. The liquid is filtered off, evaporated to dryness, and the residue heated until it melts; it is then allowed to cool, and boiled with water. A red liquid and a violet powder are obtained; the latter, after being washed and dried, constitutes "Manganese violet."

Some years ago the firm of A. Behringer, of Charlottenburg, placed on the market a violet pigment in two shades, under the name "Mineral violet," which contained manganese, phosphoric acid, and ammonia. When heated alone it gives off ammonia, becoming white. It is decomposed by potassium hydroxide at ordinary temperatures, and by ammonia on warming, with separation of manganese dioxide, and therefore appears to consist of manganous ammonium phosphate. Hence this pigment is related to, or identical with manganese violet. Its reactions suggest that it would not be fast to lime. As a matter of fact, however, it proved to be extremely stable when warmed with either calcium or barium hydroxide. Manganese violet prepared from manganese peroxide fused with phosphoric acid or ammonium phosphate may be given a bluer tint by the introduction of iron compounds.[1]

[1] Ger. P. 344156; *J. Soc. Chem. Ind.*, 1922, **41**, 149A.

The pigment is analysed by decomposing it with excess of potassium hydroxide in a retort fitted with a condenser and receiver. The ammonia is determined volumetrically, and the manganese dioxide which separates out is dried and estimated iodimetrically. The phosphoric acid in the filtrate is precipitated with magnesia mixture, and weighed as magnesium pyrophosphate.

Mineral violet is very fast to light. Washes in gum arabic remained unchanged during four years.

Violet and Red Ultramarine. These colours are obtained from blue ultramarine by the action of dry hydrochloric acid and oxygen at 150°-180°, whereby sodium is removed. Violet ultramarine, according to R. Hoffmann, is not an individual compound, but a mixture of blue and red ultramarine. It is manufactured from the blue variety by heating with ammonium chloride, and is then converted into the red form by means of hydrochloric acid. These colours have not, up to the present, acquired any great importance in commerce or in industrial applications.

VIII. Green Pigments.

(a) Natural Products.

Green Earths (Seladonite).

(Bohemian or Veronese Earth; Tyrolean Green; Seladon Green; Cyprian Earth; Terre Verte; Stone Green.)

The green earths are disintegration products of certain older minerals, chiefly of the hornblende series. In the crude state they form moist clay-like masses in a very fine state of division, which are improved by dry, or, more rarely, by wet dressing processes. They are characterised by their very fine grain, and, therefore, good spreading power and suitability for colour printing. Inferior qualities are used chiefly for industrial painting and as material for grounds in the manufacture of wallpapers, etc.; the finest qualities are employed for decorative and artistic painting. A mixture of ground green earth and white clay, under the name of "Stone green," was formerly used for the manufacture of weather-proof paints.

The green earths differ essentially from the clays and chlorites in their small content of alumina, and from the chlorites also in containing relatively small quantities of magnesia. Since they nearly always contain potash and soda, they belong to the hornblende group, and not to the augites. For a long time the colouring principle was assumed

to be a ferrous silicate. According to Delesse,[1] a Veronese green earth contained :—

Silica	51 per cent.
Alumina	7 " "
Ferrous oxide	21 " "
Magnesia	6 " "
Potassium oxide	6 " "
Sodium oxide	2 " "
Water	about 7 " "

According to Church,[2] the iron in the green earths is present as ferric silicate. The green earth contains variable amounts of nitrogenous organic matter of an acid nature.

The following figures are given for a product from Monte Baldo :—

Water, volatile at 100°	4·1 per cent.
Water, volatile at red heat	4·2 " "
Ferric oxide (Fe_2O_3)	20·3 " "
Ferrous oxide (FeO)	2·6 " "
Alumina	1·7 " "
Lime	1·1 " "
Magnesia	5·6 " "
Potassium oxide	6·4 " "
Sodium oxide	2·3 " "
Silica	51·7 " "

Gentele[3] gives the following two analyses of Bohemian and English green earths respectively, the former containing ferrous, and the latter ferric oxide :—

Green earths.	Bohemian.	English.
Silica	41·0	56·4
Alumina	3·0	2·1
Ferrous oxide	23·0	5·1
Ferric oxide	...	14·1
Calcium oxide	8·0	...
Magnesium oxide	2·0	5·9
Potassium oxide	3·0	8·8
Carbon dioxide	19·0	...
Water	...	8·8

Analysis. The varying state of oxidation of the iron in the green earths is due to the fact that they are not individual substances, but

[1] Naumann, *Mineralogie*, p. 503.
[2] *The Chemistry of Paints and Painting*, p. 212.
[3] *Lehrbuch der Farbenfabrikation*, vol. i., p. 153.

probably form a group of differently constituted isomorphous mixtures. The variety of their colour is also probably due to the varying proportion of ferrous and ferric iron. Most of the green earths are not decomposed by hot hydrochloric acid, which dissolves only the ferric oxide formed by disintegration; the more valuable qualities of this mineral are improved in tone on treatment with hydrochloric acid, as they lose their brown tint. According to Naumann,[1] green earths also exist which can be decomposed by hydrochloric acid. A Veronese green earth, decomposed by a mixture of hydrofluoric and concentrated sulphuric acid, gave a copious blue precipitate with potassium ferrocyanide and only a blue coloration with potassium ferrocyanide. In the ordinary method of silicate analysis by fusion with a mixture of sodium and potassium carbonates, all ferrous iron present becomes oxidised. Hence the ferrous iron present in green earths can only be estimated by decomposing with hydrofluoric acid, care being taken to prevent oxidation. This operation is carried out after the ferric oxide, formed by the disintegration of the earth, has first been removed by extraction with hot hydrochloric acid, and estimated. A further portion is then decomposed, and the total iron present is oxidised and estimated. The analysis is similar to that of a silicate, and silica, iron and aluminium, hydroxides, calcium, magnesium and alkali metals are determined by the usual methods. Ferrous iron is determined by the process given under iron oxide pigments (p. 495).

On ignition the green earths lose water, the iron becomes oxidised, and the resulting products are the "calcined green earths," which are fawn in colour, and are also used as painters' colours.

Lime Greens. This designation applied originally to the green copper pigments imitating natural malachite, which are stable in lime. For the last thirty years the name has been applied to particular kinds of German green earths, and to grey or white clays which have been coloured deep green by means of triphenylmethane pigments (malachite green, brilliant green). These substances are acid silicates, and exhibit the property of uniting in a particularly intimate manner with the basic dyes. For this purpose the Rhenish, Hessian, and Saxon green earths, including the "Haiger earth," are especially suitable. By means of these acid clays considerable fastness to light can be imparted to coal-tar pigments which are normally highly fugitive. When malachite green and brilliant green, unlaked and also as tannin lakes, are made up into washes with gum arabic and exposed to direct summer sunlight, they are completely destroyed within five days; but if precipitated on to green earths suitable for the purpose, they furnish lime greens in which the organic pigments become practically permanent. Four such lime greens, after exposure to direct sunlight for four years

[1] *Loc. cit.*

and seven months, had altered in tone only to the extent of assuming the well-known grey tint. Pigments of this kind fulfil practical requirements for industrial painting and also as wallpaper colours. A corresponding improvement is observed in the behaviour of the four lime greens referred to above, in mixtures with zinc white; 4 per cent. mixtures of these pigments, made up into washes with gum arabic and exposed under glass to direct sunlight, scarcely diminished in intensity within two months. Thus, in fastness to zinc white, these lime greens are vastly superior to the Prussian blues, chrome greens, zinc greens, etc., and in this respect are about equal to the ultramarines. On the other hand, the colour of a different lime green had completely disappeared in four years, the illuminated half of the test card taking on a reddish-grey shade. The same lime green, in 4 per cent. mixture with zinc white, faded in two months into reddish grey-green, and decreased considerably in intensity.[1]

It is well known that all green earths, grey clays, plastic white clays, boles, etc., do not render basic coal-tar pigments such as malachite green, brilliant greens, auramine, etc., equally fast to light. A particularly noteworthy property of the Rhenish, Hessian, and Saxon grey earths is that of rendering these basic pigments non-sensitive even towards alkalis. G. Zerr[2] states that these colour lakes have, at first, a dull dark olive-green appearance, and when dry look almost black. If, however, they are treated with dilute sodium hydroxide solution the bluish-green and vivid coloration peculiar to the lime greens appears, generally at once, and undergoes no alteration on further treatment. It would seem, therefore, that during the formation of these lime greens, alkali enters into the union of pigment and substratum. From their behaviour towards alkali a trustworthy conclusion as to their fastness to lime may be drawn.

With a decrease in the acid character of the grey earths employed, the fastness of the lime greens to light and to lime decreases. The best of the lime greens mentioned are also fast to water and spirit.

The varieties of green earth differ very considerably in their capacity for taking up colours and forming satisfactory lakes, the variation being dependent on the manner in which they are prepared for market and the nature and amount of organic matter which they contain.

The mineral *Malachite* was formerly mined under the name of "mountain green," especially in the Tyrol, for the purpose of working it up into an industrial and artists' paint. Nowadays this pigment is only found occasionally amongst artists' colours. Nearly all the modern "mountain greens" of commerce are artificial copper pigments (see p. 549).

[1] H. Wagner, *Farben-Zeit.*, 1922, **27**, 1114. [2] *Farben-Zeit.*, 1911, **16**, 14, 70, 544.

(*b*) Artificial Green Pigments.

Cobalt Green (Rinmann's Green; Zinc Green).

This pigment is prepared, as is cobalt blue, either by starting from soluble cobalt salts, treating them with sodium carbonate, mixing the precipitate with zinc oxide in suitable proportion, drying, and igniting; or else by preparing cobalt phosphate or arsenate, and treating it in a similar manner. The latter method is said to give warmer colours than the former, and to allow of the colour being produced at a lower temperature. If for one equivalent of zinc oxide more than one equivalent of cobaltous oxide is used, a dirty green colour results. Good colours are said to be obtained if for 9-10 parts by weight of zinc oxide, 1-15 parts of cobaltous oxide are employed.[1] Hence the cobalt greens, like the cobalt blues, do not consist of one individual chemical substance, and cannot be regarded as pure cobalt zincate. The cobalt greens are put on to the market in three shades, namely, "light," "medium," and "dark," which differ also in tint, varying from bluish- to yellowish-green. Like cobalt blue they can be looked upon as substratum colours, containing more or less zinc oxide. The mean percentage composition is stated to be 88 per cent. zinc oxide and 12 per cent. cobaltous oxide. According to Wagner a dark cobalt green contained 71·93 per cent. zinc oxide, 19·15 per cent. cobaltous oxide, 8·23 per cent. phosphoric acid, and 0·69 per cent. sodium oxide.

Analysis. Cobalt greens dissolve when heated with hydrochloric acid, giving a red solution. On continued boiling with the darker varieties, potassium hydroxide is coloured light blue, and ammonium carbonate solution a very beautiful violet. Phosphoric acid appears to occur only rarely in the cobalt greens manufactured at the present day. It was present in only one out of twelve samples examined.

For quantitative analysis the pigment is dissolved in the minimum quantity of nitric acid, diluted, and potassium hydroxide added until a slight precipitate forms. This is cleared with acetic acid, and to the clear or filtered solution a large excess of potassium nitrite solution containing acetic acid is added. The precipitate is allowed to settle for some hours and is filtered through a Gooch crucible fitted with a paper disc. After washing with potassium nitrite solution and finally alcohol, the potassium cobaltinitrite is dissolved in hydrochloric acid and the cobalt precipitated as sulphide or determined in other ways (*cf.* p. 325). Alternatively, adjusting the acidity of the hydrochloric acid solution, the cobalt may be precipitated as $Co(NH_4)PO_4$ and ignited to $Co_2P_2O_7$. Nickel, if present, is precipitated from the filtrate, after boiling with excess of hydrochloric acid, by means of potassium hydroxide, and is converted into nickelous oxide. Zinc is precipitated from the filtrate

[1] *Cf.* Munkert, *Normalfarben*, p. 151.

as sulphide, and, after ignition, determined as oxide. The zinc sulphide may be redissolved in hydrochloric acid and reprecipitated as zinc ammonium phosphate.

Of the methods examined by Fox and Bowles,[1] (1) precipitation of zinc in ammonium thiocyanate solution, (2) precipitation of cobalt with α-nitroso-β-naphthol, (3) precipitation of cobalt as cobalt ammonium iodide, (4) precipitation of cobalt as cobalti-nitrite, the last has been found to be most satisfactory. They give the results of the analysis of a good sample of this pigment as follows:—CoO, 8·7 per cent., ZnO, 89·8 per cent., and loss on igition 1·4 per cent.

Fastness to Light and Compatibility in Mixtures. The cobalt greens are permanent in light. They are unstable in mixtures with zinc yellow, yellow ultramarine, or zinc green. Cobalt green is much more stable towards zinc white than are the ultramarines; 10 per cent. mixtures in the form of water colours exposed to light under glass underwent practically no change in two months. This behaviour is explained by the fact that the cobalt greens possess to some extent the composition of zincates.

Gellert Green, a variety of cobalt green, is obtained by roasting and igniting metallic cobalt with 4-5 parts of saltpetre and 8-10 parts of zinc oxide.

On account of their relatively high cost these pigments are chiefly used as artists' colours.

Manganese Green.

(Cassel Green; Rosenstiel's Green; Baryta Green.)

This pigment, which is but little used, and is said to be sensitive to moisture, is obtained by heating a mixture of oxides of manganese, barium nitrate and heavy spar, or kaolin. Barium peroxide is also used.

The Green Chromium Pigments.

The trade name "chrome green" was formerly applied to chromium sesquioxide, Cr_2O_3, or to the green colours closely related to it. Later however, the name was also applied to the cheaper green mixtures prepared from chrome yellow and Prussian blue, from which the true chrome green is now distinguished by the name "chrome oxide green."

Chrome Oxide Green (Dull or Non-glazing.)

The technical methods of preparing "dull chrome oxide green" depend on the reduction of chromates, and aim at producing a pigment of the highest possible brilliance and suitability for colouring purposes. Like the varieties of mercuric oxide, cadmium yellow, and the red iron colours, chromic oxide exhibits marked differences in density and size

[1] J. J. Fox and T. H. Bowles, *The Analysis of Pigments, Paints, and Varnishes*, 1927, p. 113.

of grain and therefore in shade, according to the method of preparation, temperature, nature of additions, etc., used in its manufacture. According to Dieterich, sulphur, soft wood-charcoal, potato starch, and paper-makers' wood-pulp serve as reducing agents; while Casali states that gypsum and picric acid are also used. The products of these various methods of preparation exhibit considerable differences in tone. The colour obtained from mercurous chromate is the most beautiful, but it is too expensive. Approaching the latter is the colour obtained by means of picric acid, whilst that produced with sulphur is duller.[1] On the other hand, the green product which results from the decomposition of ammonium bichromate on heating, is not the oxide Cr_2O_3, as is generally stated, but a mixture of the latter with the dark brown chromium dioxide CrO_2.

Analysis. Chrome oxide green, prepared in one of the above ways, is usually almost chemically pure chromic oxide, Cr_2O_3, as the by-products formed during the manufacture are easily removed by water or acids. Adulterants are scarcely ever present. Its shade alone serves to distinguish it from the green vermilions, green earths, etc.; unlike the latter it is stable on ignition and on warming with alkalis. It is quite insoluble in acids, but can be decomposed by prolonged boiling with strong nitric acid and potassium chlorate. This method is useful in the examination of such a mixture as chrome oxide green with lead chrome and barytes: the chrome yellow is first decomposed with strong hydrochloric acid, the mixture largely diluted with water and the insoluble barytes and chrome green filtered off. The chrome green is then separated by boiling this residue with strong nitric acid and potassium chlorate. The valuation is carried out by fusing with potassium nitrate and sodium carbonate, dissolving the melt, and separating the alumina and iron. After reducing by alcohol and hydrochloric acid, the silica is separated by evaporating to dryness three times, and the chromium precipitated in the filtrate as hydroxide, ignited, and weighed as Cr_2O_3.

"Dull" chrome oxide green was formerly used more especially for glass and porcelain painting, also for printing bank-notes, as it cannot be reproduced by photographic processes; a further use was for printing wallpaper. For a long time past the consumption of this colour has largely diminished, owing to its comparative dearness and lack of brilliance. W. J. Palmer[2] has pointed out the special value of chromium oxide green as a pigment on account of its great permanency to sunlight and its chemical stability. It is still used to a large extent as an artists' colour. It is a pronounced body colour, and is stable in mixtures with other pigments.

[1] For details of the manufacture, see Zerr and Rübencamp, *Colour Manufacture*, p. 231.
[2] *J. Oil and Col. Chem. Assoc.*, 1925, 8, 91.

Guignet's Green.

(Emerald Oxide of Chromium; Chrome Green; Vert de Guignet; Viridian; Victoria Green.)

Guignet's green is made by heating a mixture of 1 part of potassium or sodium bichromate and 3 parts of crystallised boric acid in a muffle at about 700°. Reduction of the chromate takes place with the formation of chromium metaborate together with alkali borate. The former, on further heating, is converted into an alkali-chromium pyroborate which is dark green in colour and, on hydrolysis, gives Guignet's green. Besides this main reaction certain secondary reactions also occur.

Since all commercial samples of Guignet's green contain boric acid, Shipton[1] assumed that it was an integral component of the pigment; on the other hand, Guignet and Salvétat recognised that the boric acid was a technical impurity, and put forward the formula $Cr_2O(OH)_4$, which requires 19·1 per cent. of water. Scheurer-Kestner subsequently found about 15 per cent. of water, corresponding to the formula $Cr_4O_3(OH)_6$. L. Wöhler and W. Becker[2] have confirmed this formula for the commercial Guignet's greens. On the other hand, they obtained from ammonium bichromate greens with a maximum water-content of 37 per cent. Wöhler then prepared a green, insoluble in hydrochloric acid and possessing the tone of Guignet's green, by heating precipitated chromium hydroxide with water under pressure, the product being free from all the secondary constituents and impurities present in the commercial Guignet's greens.

The investigations into the constitution, methods of formation and analysis of Guignet's greens, begun in 1908 by A. Eibner and O. Hue. have given the following results:—The commercial products "pale" and "dark" Guignet's greens are not chemical individuals but mixtures of (1) Two chief constituents insoluble in acids, viz.—the hydrates $Cr_4O_3(OH)_6$ and $Cr_4O(OH)_{10}$, on which the characteristic shade depends, and the following secondary constituents present in small quantities: (2) Chromium sesquioxide, Cr_2O_3, which is formed when the temperature exceeds 700° and the charge is in that way partly "overburnt." (3) The brownish-black chromium peroxide, probably Cr_3O_6, which is chiefly formed when too little boric acid is present. (4) Alkali, occluded by the chromium hydroxide, which is very difficult to remove. In addition, a fifth constituent, chromium metaborate, occurs in many samples of Guignet's green as an intermediate product; it is soluble in acids. Boric acid is to be looked upon as a technical impurity which, on the large scale, cannot be completely removed; some of the newest brands

[1] *Dingl. polyt. J.*, 1865, **176**, 315.
[2] *Z. angew. Chem.*, 1908, **21**, 1600; *J. Soc. Chem. Ind.*, 1908, **27**, 865.

showed only a small content of this component (6·82, 4·29, 1·95 per cent.). Some Guignet's greens contain, as further technical impurities, small quantities of alkali chromates and iron compounds.

According to more recent researches by Wöhler and Dierksen,[1] from a study of the isomerism of Guignet's green the brilliance of this pigment has been found to increase progressively with reduction in the water content of the chromium hydroxide gel. The function of boric acid or silicic acid employed on the large scale is solely that of producing flocculation.

In commercial greens prepared from alkali bichromates the content of water varies between 15 and 22 per cent., and in those from ammonium bichromate, between 25 and 43 per cent.; a portion of the water is present in the adsorbed state. Guignet's greens are therefore hydrogels, like the Prussian blues. Under certain experimental conditions they pass into hydrosols (colloidal solutions of Guignet's green).

The greens prepared from ammonium bichromate, when made on the small scale, are free from Cr_2O_3 and Cr_3O_6 and, in consequence, possess a much higher glazing power than the commercial greens. Moreover they are free from alkali. The green which L. Wöhler[2] obtained by heating precipitated chromium hydroxide with water under pressure is the purest and most highly glazing Guignet's green. It corresponds most nearly, without regard to its character as a hydrogel, to the formula advanced by Scheurer-Kestner.[3]

Analysis. From the foregoing statements it is clear that the method of analysing Guignet's greens adopted up to the present, by fusing with sodium carbonate and potassium nitrate, does not lead to the determination of all the constituents. In the first place the adsorbed water should be estimated by determining the loss of weight on standing in an exsiccator over sulphuric acid. Further, in estimating the total water-content it must be borne in mind that chromium hydroxides, when heated in the air, are converted into peroxides, which decompose into Cr_2O_3 and oxygen only on the application of a very strong red heat. The substance must therefore be heated over the blowpipe until the black mass has become bright green. Before estimating the boric acid it is necessary to ascertain whether any portion is present in the combined state as chromium metaborate; this is done by extracting with hydrochloric acid. The boric acid content is determined by difference as follows:—After ignition, the green residue is weighed and is then treated with a mixture of hydrofluoric and sulphuric acids on the sand-bath, and the boron volatilised.

[1] *Z. angew. Chem.*, 1926, **39**, 13.
[2] *Loc. cit.*
[3] For further researches on the composition of Guignet's green, see Eibner and Hue, *Farben.-Zeit.*, 1910, **51**, 2106, 2157, 2213, 2268, and 2319; also, L. Wöhler and W. Becker, *Z. angew. Chem.*, 1911, **24**, 484; *J. Soc. Chem. Ind.*, 1911, **30**, 559.

After washing out the alkali salts, the boron-free oxide is then dried and weighed.

Potassium is estimated by heating the ignited sample with a mixture of hydrofluoric and sulphuric acids as described above, lixiviating the residue with water, and precipitating with ammonium hydroxide. The filtrate is evaporated and the residue heated until the ammonium salts are driven off; it is then taken up with sulphuric acid, and the potassium determined as sulphate.

According to Fox and Bowles[1] the chromic oxide greens are difficult to bring into solution and the best method of attacking them is to fuse with sodium peroxide in a nickel crucible. One g. of the pigment is thoroughly mixed with 3 g. of sodium peroxide in a nickel crucible provided with a lid. Guignet's green should be ignited before mixing with the sodium peroxide in order to drive off some of the combined water. The mixture is heated until fusion occurs, and maintained at a dull red heat for fifteen minutes on the covered crucible. On cooling, a crust separates on the top of the melt; at this stage another gram of sodium peroxide is added and the mass is again fused at low redness for a few minutes. When cool the crucible is placed in an evaporating dish, about 100 c.c. water added and the melt boiled for at least ten minutes. The crucible is then washed out, 5 g. of solid ammonium carbonate added, and the mixture heated to boiling. The liquid is diluted, filtered hot, and the insoluble residue, if any, is washed well. The filtrate contains all the chromium as sodium chromate together with borates, silicates and phosphates if present. The chromium may be estimated volumetrically in the usual manner.

A sample of Guignet's green analysed by Fox and Bowles gives:—

Chromium oxide	70·2 per cent.
Boric oxide	5·4 "
Silica	1·0 "
Alumina	0·9 "
Sodium oxide	2·1 "
Combined water	20·2 "

The estimation of the chromium peroxide is still uncertain, since it can be decomposed by hydrochloric acid only with great difficulty, the iodometric method is scarcely applicable, and the peroxide must be estimated by measuring the oxygen evolved on heating the pigment in an indifferent gas.

Chromium Phosphate Greens.

Arnaudon's Green is prepared by stirring up 128 parts of ammonium phosphate and 149 parts of potassium bichromate with water to a paste, and heating the mixture to 170°-180°, whereby reduction takes place; the temperature must not rise above 200°. The green mass obtained is

[1] J. J. Fox and T. H. Bowles, *loc. cit.*, p. 100.

lixiviated with water. The green produced in this way is not much inferior in beauty to Schweinfurth green. When heated in a tube it does not, like Guignet's green, become black, but violet-red, and green again on cooling. This colour is probably a basic chromium phosphate.

Schnitzer's Green is of similar composition to the above, but crystallised sodium phosphate is used in its preparation.

Mathieu Plessy's Green is prepared by warming together 10 kg. of potassium bichromate dissolved in 10 kg. of boiling water, 3 litres of calcium phosphate solution containing 6·5 per cent. of phosphoric acid, and 5 kg. of sugar or starch-sugar as a reducing agent.

Ultramarine Green is the intermediate product of the indirect manufacture of blue soda-ultramarine, and the end-product of the raw-burning process in the production of sulphate-ultramarine. It does not possess the depth and brilliance of the blue ultramarines, and is also duller than the Permanent greens. It is, however, manufactured for use as a lime wash, for printing wallpaper, etc. Ultramarine green varies, according to the duration of burning and the temperature, from yellow-green to blue-green, and also in depth of shade. It differs from blue ultramarine, *inter alia*, in possessing a higher content of sodium.[1] (For analysis, see Ultramarine, p. 530.)

(*c*) Green Mixture-pigments of Chrome Yellow and Paris Blue.

Brunswick Green.

(Chrome Green; Milori Green, etc.)

This green is a mixture of chrome yellow, Prussian blue, and barytes, and comes into commerce in a variety of shades ("pale," "middle," "deep," and "ex-deep") according to the proportions of the constituents. It is very largely used, both as an oil and water colour, especially the former. It must not be mistaken for the pigment, a compound of copper, originally known under this name.

It can be prepared by grinding together the several pigments in the dry state, also (and this is the better method) by precipitating the blue and yellow simultaneously on the barytes.

Brunswick green in admixture with other pigments exhibits the properties of its component parts, hence, for example, it cannot be used with lime as both the blue and the chrome would be affected. (See "Prussian Blue" and "Chrome Yellow.")

[1] R. Hoffmann, *Ultramarin*, p. 88.

Analyses of Chrome Greens (Holley).

	Light Chrome Green.	Medium Chrome Green.
Moisture	0·20	0·10
$PbCrO_4$	16·57	16·67
$PbSO_4$	5·80	5·29
Prussian blue	5·98	6·80
$BaSO_4$	68·22	66·72
Al_2O_3	1·40	1·94
SiO_2	1·71	1·66

Owing to the varying composition of chrome green, due to the method of manufacture, a chemical examination is of small value in determining the quality of the green. The usual tinting strength determination should be made and the pigment examined microscopically to determine whether the green is a product made by precipitating two pigments together or by mixing the blue and yellow pigments after separate precipitation. A good green will show the presence of green and blue particles but no yellow, while a poor green will show yellow and blue particles mixed with green. An analysis of the chrome green may be made as follows:[1]—

Moisture. Two g. of the sample is heated for two hours at 105°.

Insoluble Residue. One g. of the sample is heated at a very low temperature until the blue colour has been completely destroyed keeping the temperature low so that the iron or lead chromates are not made insoluble. After cooling 30 c.c. of concentrated hydrochloric acid is added and the whole boiled until all the soluble constituents have passed into solution, which may be hastened by the addition of a few drops of alcohol. After dilution of the sample with water, it is boiled and filtered, and the insoluble residue washed and weighed. This residue is occasionally examined for silica, barytes, and alumina, in the manner given under the analysis of a white pigment.

Lead. The excess of acid present in the filtrate from the insoluble residue is almost neutralised with ammonia and the lead precipitated by sulphuretted hydrogen and estimated in the usual manner.

Iron, Aluminium, and Chromium. The filtrate is treated in the usual manner for the precipitation of iron, aluminium, and chromium hydroxides. The precipitate is filtered off, washed, dissolved in hydrochloric acid, and made up to a definite volume. In one portion the mixed hydroxides are precipitated with ammonia, filtered, washed, and weighed together. Another portion is treated in a flask with excess of potassium hydroxide and bromine water until the iron hydroxide has assumed its characteristic reddish-brown colour. The

[1] Gardner and Schaeffer, *Analysis of Paints and Painting Materials*, 1911, p. 36.

iron hydroxide can be filtered off and estimated volumetrically. The filtrate from the iron precipitate is acidified with nitric acid and the alumina precipitated with ammonia. Chromium is determined in the filtrate by reduction to a chromic salt with hydrochloric acid and alcohol, precipitating with ammonia and weighing as oxide.

Calcium and Magnesium are determined in the filtrate from the iron, aluminium, and chromium precipitation.

Sulphuric Acid. One g. of the sample is dissolved in 30 c.c. of concentrated hydrochloric acid (after ignition until the blue is completely decomposed, as before stated), diluted with water, boiled, filtered and washed. If lead sulphate is present, the acid filtrate is neutralised with solid sodium carbonate, an excess added and the liquid boiled for half an hour. The insoluble carbonates are filtered off and the sulphate is determined in the filtrate by precipitation with barium chloride in the usual manner.

Nitrogen may be determined by the Kjeldhal-Gunning method.

The Prussian blue present is calculated by multiplying the iron found by 3·03 or the nitrogen found by 4·4. The sulphate is calculated to lead sulphate and calcium sulphate, should calcium be present, and the chromium to lead chromate.

Zinc Greens.

The name "Zinc green" is now applied exclusively to mixtures of zinc yellow and Prussian blue, that is, to "zinc-yellow greens." Like the chrome greens, they contain varying quantities of heavy spar or blanc fixe and are likewise prepared in many different shades, which are purer but also paler than the chrome greens. The palest varieties possessing a yellow tint are known as "parrot greens." (Varieties of Schweinfurth green also pass under this name.) The so-called "blueing" of zinc greens, when used as oil colours, is due to faulty preparation, and is caused by the Prussian blue making its way to the surface. The zinc greens are just as unstable towards lime as the chrome greens, but, on the other hand, are much faster to light.

Analysis. Chrome greens and zinc greens are decomposed by potassium hydroxide. The zinc yellow in the zinc green is completely dissolved, so that the precipitate consists only of heavy spar and hydrated ferric oxide, all the zinc, together with the potassium ferrocyanide, being in solution. Zinc chrome is not reprecipitated when acetic acid is added and thus differs from Brunswick green. The zinc in solution can be recognised by a white precipitate on addition of ammonium sulphide.

The procedure in the quantitative analysis of chrome and zinc greens is regulated according to the constituent to be estimated (see pp. 484 and 489).

Green Vermilion, English Green, Mineral Green. These colours are closely related to the chrome greens, and are usually prepared by treating Prussian blue, rendered soluble by oxalic acid, with a solution of potassium bichromate, and then adding a solution of lead acetate. If barium salts are used for precipitation, shades similar to the zinc greens are obtained.

According to G. Wendt, a green vermilion containing no yellow is prepared by adding 1 part of a solution of potassium ferrocyanide saturated in the cold to 15 parts of oxalic acid, and warming on the water-bath until the dark blue turbidity which forms at first has changed to a sea-green. This mixture is then poured into a solution of 15 parts of ferrous sulphate saturated in the cold. The name "green vermilion," being a spurious substance designation, should be abandoned.

Fastness to Zinc White (of the chrome greens and zinc greens). Since both Prussian blues and chrome yellows in the form of water colours are extraordinarily sensitive to sunlight when mixed with zinc white, and zinc yellow under similar conditions is also unstable, it is to be expected that the chrome greens and zinc greens will exhibit the same defects. This is the case:—1 per cent. mixtures of chrome greens and zinc greens with zinc white faded considerably within a month, and at the same time assumed a strong blue tint. The yellow component is therefore more rapidly destroyed than the blue, owing to the reversibility of the light reaction in the latter case.

(*d*) The Green Copper Pigments.

These pigments, although little used in ordinary paints and artists' colours, are in demand on account of their poisonous properties in antifouling compositions for ships' bottoms, and in paint for use in the tropics to prevent attacks of the white ant.

1. *Imitation Native Malachite Greens.*

Mountain Green was formerly prepared by precipitating a boiling solution of alum and copper sulphate with a hot solution of sodium or potassium carbonate (Mierzinski). The Mountain green obtained according to Gurth's method contains added Schütt yellow. Varieties of mountain green blended with white clay, heavy spar, etc., are known under the names "Alexander green," "Glance green," and "Napoleon's green."

Green Verditer is an artificial malachite, prepared by precipitating solutions of copper with potassium and sodium carbonates. It is nearly obsolete.

Lime Green (Earth Green) (*vide* p. 538).—This name was originally given to a pigment obtained by precipitating copper sulphate solution with chalk, or milk of lime. It is not stable.

Bremen Green is the intermediate product in the preparation of Bremen blue (p. 524).

Brunswick Green was originally obtained by treating copper sulphate with common salt, and precipitating with milk of lime; in this case it is a basic copper chloride. When precipitated with sodium carbonate it possesses the composition, $CuCO_3 . Cu(OH)_2$. At the present day the name has been transferred to mixtures of chrome yellows and blue, to which the names "Prussian green" and "Victoria green" are also applied. The name "Brunswick green" is, however, also applied to Bremen blue and to an arsenical copper green containing no acetic acid, as also to a variety of Schweinfurth green.

Erlau Green is prepared in a similar way to the old Brunswick green, by adding a mixture of copper sulphate and common salt to milk of lime, washing the precipitate obtained, and treating it with a solution of neutral potassium chromate. Vienna white or heavy spar is added to it.

Bolley's Green is a copper borate dehydrated by heating to redness. It possesses good covering power and is applied as an oil colour. Little use is made of it at the present day.

Gentele's Green, tin-copper green, is obtained either by precipitating copper sulphate solution with stannous chloride and washing and drying the precipitate, which is white at first but later becomes green; or else by using sodium stannate and washing the precipitate (which is at first orange-yellow), whereby it gradually becomes green.

Elsner's Green is a mixture of tin-copper green and fustic decoction.

2. *Verdigris.*

These colours include the true verdigris (Verdit, Verdet, Grünspan), which occurs in two varieties: as "Neutral blue" or "Crystallised Verdigris," in the form of "grapes," and as "Basic Verdigris" in balls. At one time it was prepared by the action of wine residues on copper; acetic fermentation sets in and the immediate product is neutral copper acetate. At the present time vinegar is used, or calcium or sodium acetate is allowed to act on copper sulphate, or else copper carbonate is dissolved in vinegar. Crystallised verdigris approaches the composition, $Cu(C_2H_3O_2)_2$, but it also contains basic acetate. The composition $Cu(C_2H_3O_2)_2 . 2Cu(OH)_2$ is ascribed to the basic green-coloured verdigris. Common verdigris contains 13-25 per cent. of water. Three kinds of verdigris, English, French, and German, are recognised. Verdigris should dissolve completely in ammonium

hydroxide, or at any rate not leave more than 2-3 per cent. of residue. It is also readily soluble in all acids without effervescence. Additions of chalk, gypsum, and heavy spar are sometimes made. Verdigris is a glazing colour; it is very unstable, and its consumption is decreasing.

Analysis. In testing for metals other than copper it is well to ignite the verdigris, dissolve the residue in hydrochloric acid and apply the usual group tests. Solution of the verdigris in hydrochloric acid with effervescence would point to the presence of chalk, while barytes would be left as an insoluble residue. Sulphate present in the hydrochloric acid solution should be estimated by barium chloride and probably means the presence of gypsum which the presence of calcium would confirm.[1]

Casselmann's Green is a basic verdigris obtained by mixing a boiling solution of sodium acetate with copper sulphate. Next to Schweinfurth green it is the most beautiful copper colour. It has the composition $CuSO_4 . 3Cu(OH)_2 . 4H_2O$.

The so-called *Saxon Verdigris* approaches the old Brunswick green in composition, and is formed by precipitating a mixture of copper sulphate and common salt with milk of lime. It contains gypsum or Vienna white.

3. *Arsenic Greens.*

These colours consist of either basic arsenite or arseno-acetate of copper, with or without additions. Included in the former class is *Scheele's Green*, which was originally prepared by treating a solution of copper sulphate with a solution of white arsenic in sodium carbonate, and then adding caustic soda solution until copper could no longer be detected in the filtrate from the green precipitate which was formed. This green varies in colour from canary-green to dark green, according to the amount of arsenious acid it contains.[2] As a pigment it has gone out of use.

Another pigment sold under the name of *Scheele's green* is obtained by precipitating a dilute solution of copper sulphate with an alkaline solution of arsenic. It has fairly good covering power, and can be used as a water and oil colour as well as for lime wash.

Emerald Green (usually called *Schweinfurth Green* in Germany). Some fifty names have been employed for the designation of this green in its various pure and adulterated forms, and as prepared by the older or newer methods. Some of these indicate its origin, whilst others are fancy names, the object of which has been to disguise the

[1] For the estimation of cuprous copper in copper paints consult C. J. Hough, *J. Soc. Chem. Ind.*, 1919, **38**, 914A.

[2] *Cf.* Zerr and Rübencamp, *Colour Manufacture*, p. 227.

poisonous character of the colour. The older names for emerald green are:—Mitis, Vienna, Paris, Verdigris green (for an emerald green prepared according to the old method, from verdigris), Emperor, New, Mineral, Original green, Vert Paul Veronese, etc. It occurs under the last name as an artist's colour. The use of emerald green has been on the decrease of late years.

The modern method of preparing emerald green consists, in the first place, in mixing a hot solution of white arsenic in sodium carbonate with the calculated quantity of copper sulphate solution. Dirty green copper arsenite is formed. After some time, the required quantity of acetic acid is added, with stirring, at a temperature of about 80°, and the solution is then diluted with water until the temperature has fallen to 20°. In about an hour the formation of the green, which takes place with evolution of carbon dioxide, is complete. The beauty of the shade depends on the manner in which crystal formation takes place. Emerald green is the most beautiful green inorganic colour known. The more arsenic it contains, the paler it is. It is a double salt of copper arsenite and copper acetate and has the formula, $Cu(C_2H_3O_2)_2 . 3CuAs_2O_4$.

Analysis. Pure emerald green dissolves in dilute acids, the caustic alkalis, and in ammonium hydroxide, leaving no residue, indicating the absence of china clay, barytes, etc., and with the exception of malachite all the copper green pigments should dissolve in dilute hydrochloric acid without effervescence. The solution should not give any precipitate on the addition of excess of ammonia, indicating the absence of salts of aluminium, calcium, magnesium, etc. On boiling with caustic soda or potash it is decomposed and the copper precipitated as red cuprous oxide. When heated with dehydrated sodium carbonate in a tube it evolves an odour of cacodyl.

The presence of chrome yellow may be detected[1] by dissolving in hydrochloric acid (a white precipitate is often formed which disappears again on the addition of a large quantity of water), diluting with water, and adding sulphuric acid. The lead sulphate is filtered off, and the filtrate boiled, with addition of alcohol; on adding ammonium carbonate, chromic hydroxide is precipitated.

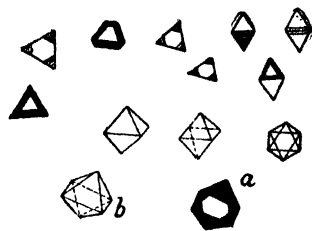
The copper is estimated by dissolving the emerald green in hydrochloric acid, treating the solution with excess of ammonium carbonate, filtering off any precipitate formed (alumina, calcium, magnesium), and precipitating the copper in the boiling filtrate with sodium hydroxide.

The microscopic examination of the colour is also of importance. This is best carried out by mixing it with a drop of glycerin on a slide, without grinding, and laying a cover-glass over the mixture; the

[1] Bolley-Stahlschmidt, *Handbuch der techn. chem. Untersuchungen*, 1889, p. 352.

magnification required with dark greens is about 200, with lighter greens from 400-500. Heavy spar and light spar (naturally occurring ground gypsum) are easily recognised by this examination. The presence of octohedra of arsenious oxide (Fig. 50) indicates that the colour is a verdigris green, prepared by the verdigris method.[1]

FIG. 50.

S. Avery and H. T. Beans[2] have shown that the usual methods for estimating the soluble arsenic trioxide in emerald green, depending essentially upon extraction with water, are impracticable, and recommend the following procedure:—1 g. of the colour is heated for five minutes with 25 c.c. of sodium acetate solution (12·5 g. in 1000 c.c.); the solution is cooled, made up to 100 c.c., and an aliquot portion titrated with iodine solution. Sodium acetate largely prevents hydrolysis of the copper arsenite.

J. K. Haywood[3] has modified the above method for the estimation of the total amount of arsenic trioxide. The latter method gives very good results if the samples of emerald green are pure, but if much free arsenious oxide is present the results are too low. The following method is therefore adopted:—2 g. of an average sample is powdered in an agate mortar, and 0·3-0·4 g. of the powder treated in a beaker with 25 c.c. of water; concentrated hydrochloric acid is then added, drop by drop, with constant stirring, until the colour is all dissolved. Under these conditions free arsenious oxide remains insoluble and is filtered off and washed; the arsenious oxide in the filtrate is estimated by Avery and Bean's method. The filter paper and its contents are washed out of the funnel into a beaker, treated with 5 g. of sodium bicarbonate, boiled for five to ten minutes until the arsenious oxide is completely dissolved, the solution cooled, acidified in presence of a drop of methyl orange, then rendered alkaline again with sodium bicarbonate, and after addition of starch solution, titrated with iodine solution.

When free arsenious oxide is present, S. Avery[4] recommends the following treatment:—The sample is gently heated with about $N/2$ hydrochloric acid, using 5-10 c.c. for every 0·1 g.; if the substance does not dissolve completely, a cold saturated solution of sodium acetate (about 3 g. of the salt for every 0·1 g. of the sample) is added, and the mixture boiled until all the arsenious oxide is dissolved. All the

[1] Cf. *Z. angew. Chem.*, 1888, **1**, 47.
[2] *J. Amer. Chem. Soc.*, 1901, **23**, 111.
[3] *Ibid.*, 1903, **25**, 963.
[4] *J. Amer. Chem. Soc.*, 1903, **25**, 1096.

copper must be in solution before the acetate is added. When the substance is completely dissolved, alkali tartrate and solid bicarbonate are added, and the dilute solution then titrated in the usual manner.

For the analysis of copper arsenite pigments, in the absence of calcium, etc., the method of Peters and Fielding[1] is rapid and accurate. They precipitate the copper as oxalate, which is determined by titration with potassium permanganate, the arsenic being determined iodometrically in the filtrate.

About 0·25 g. of the pigment is weighed into a small beaker, less than 1 c.c. of sulphuric acid (1 : 10) is added and, maintaining the volume at 50 c.c. the liquid is boiled for two minutes. While hot 2 g. of crystallised oxalic acid is added, the liquid heated again to boiling and left to stand overnight. The precipitated copper oxalate is filtered on to an asbestos filter and washed with a little water to remove the arsenic completely. It is mixed with a convenient amount of water, 5 or 10 c.c. sulphuric acid (1 : 1) added and the mixture heated almost to boiling. The oxalic acid is titrated with standard permanganate. The filtrate from the copper oxalate is neutralised by dry sodium bicarbonate and the arsenic determined by standard iodine.

Analyses of Emerald Green. Forty-four commercial samples examined by L. L. van Slyke and W. H. Andrews[2] in 1902, contained :—

	Mean.		
55·39 to 61·40 =	57·10	per cent.	As_2O_3
0·61 „ 1·35 =	1·01	„	As_2O_3, soluble in water
27·03 „ 30·79 =	29·41	„	CuO
50·60 „ 57·60 =	55·10	„	As_2O_3, combined with copper.

The arsenic greens known as *Soda greens* are obtained by neutralising with sodium carbonate the mother liquor containing white arsenic, acetic acid, and dissolved emerald green, which is produced in the preparation of the latter. If the neutralisation is carried out with milk of lime, the resulting products are the *Lime-arsenic greens.*[3]

Neuwied Green is a mixture of emerald green with varying quantities of gypsum, heavy spar, or blanc fixe. It is prepared by a process similar to one of the old methods for obtaining emerald green. It is now only rarely found in commerce.

Compatibility in Mixtures.—As already mentioned, emerald green very rapidly undergoes double decomposition with cadmium yellow, orange, and red, copper sulphide being found. Partial discoloration of mixtures with ultramarine, Saturn red, and vermilion has been observed to take place within a year.

[1] *Ind. Eng. Chem.*, 1916, **8**, 1114.
[2] *New York Agricultural Exp. Sta., Geneva, N.Y.*, Bull. No. **222**, 1903, p. 265.
Zerr and Rübencamp, *Colour Manufacture*, p. 219.

IX. Brown Pigmfnts.

(*a*) Natural Products.

Umber, Umber Brown (Mineral Umber).

(Velvet Brown ; Chestnut Brown ; Manganese Velvet Brown ; Burnt Umber.)

Umber is a naturally occurring brown pigment, similar in composition and properties to ochre and sienna, but containing a larger proportion of manganese. It is found in many parts of England, in France, Italy, etc , while the finest qualities come from Sicily and Cyprus. It comes into commerce in two forms, "raw" and "burnt," the latter possessing a deeper and more reddish tint than the native variety. As pigments the umbers work well both in oil and water, they are quite permanent and can be mixed with all other pigments without being in any way affected.

They are decomposed by prolonged boiling with concentrated hydrochloric acid and can be examined by the methods used for ochres and iron oxides (p. 495). The manganese is best estimated iodometrically.

Cologne Earth, *Cassel Brown* are pigments of natural origin, but contain lignite or other organic matter. The lignite is soluble in warm caustic potash. These pigments vary greatly in composition and are therefore of little use.

Vandyke Brown is also a natural product, partly organic, but imitations made from lamp black, red oxide and yellow ochre are sold under this name. These products are easily recognised by the floating particles of carbon black on admixture with water.

Analysis. The methods given under the Siennas on p. 471 are applicable to the Umbers.

(*b*) Artificial Products.

Berlin Brown is produced by charring Prussian blue, and is a mixture of ferroso-ferric oxide, ferric oxide, and charcoal. It is only used as an artist's colour.

Florentine Brown, also known as Vandyke red and Hachette brown, is copper ferrocyanide. Its permanence in the light is not as great as that of the unmixed Prussian blues. As regards its compatibility with other pigments, sufficient data are not yet available.

X. Black Pigments.

Bone Black, Drop Black, Ivory Black, Lampblack, Vegetable Black, Graphite, Wood Charcoal, Vegetable Charcoal, Vine Black, Mineral Black, Black Oxide of Iron, Black Oxide of Manganese.

The usual black pigments are those consisting of carbon, existing either in crystalline form (graphite) or the amorphous form which includes all the many artificial carbon blacks. Black enamels contain coal tar and asphaltic mixtures and are described in the section on Paint Vehicles, Japans and Varnishes (pp. 563 *et seq.*).

Fox and Bowles classify black pigments for purposes of analysis as follows:—

(*a*) Blacks prepared by charring organic matter: bone black, drop black, ivory black, charcoal, mineral black (from waste coal).
(*b*) Blacks from deposited carbon, or soot-blacks: lampblack, vegetable black, and carbon black.
(*c*) Naturally occurring products: black oxide of iron, Fe_3O_4, black oxide of manganese, MnO_2, mineral black (black slate or clay shale), natural graphite.
(*d*) Artificial graphite.
(*e*) Black or blue black organic dyes.

Analysis. The following methods are, in main, those given in the "Interim Report on Methods of Analysis of Coal," issued by the Fuel Research Board of the Department of Scientific and Industrial Research, to which reference should be made where greater detail is required. (See also Vol. I. pp. 327-340.)

Moisture. From 1 to 2 g. of the pigment is weighed in a shallow weighing vessel provided with a well-fitting cover, and heated, uncovered, for one hour at a temperature of 105°-110°. The dish is then covered, allowed to cool in a desiccator over sulphuric acid, and weighed. The loss in weight is expressed as "moisture."

Oily Matter. This may be determined by extraction of a suitable quantity of pigment in a Soxhlet apparatus with ether, chloroform, carbon disulphide, or other suitable solvent. The solvent is finally evaporated off in a tared vessel and the extract is dried at a temperature of 70° and weighed. Gas blacks usually contain considerable proportions of oily matter.

Ash. From 1 to 2 g. of the pigment is weighed in a shallow platinum, silica, or porcelain dish, approximately 1 cm. deep by 5 cm. diameter, and heated at first slowly to prevent mechanical loss and finally at a temperature of 750°-800° in an oxidising atmosphere in

a muffle furnace for one hour or until constant in weight. If graphitic carbon is present, it is extremely difficult to burn in a muffle furnace, unless a free supply of air is allowed to pass over the dish. Should carbonates be present, the ash is mixed with a small amount of ammonium carbonate and again ignited, thus reconverting to carbonate any oxide which may have been decomposed. The ash is examined for SiO_2, Ca, Mg, and phosphoric acid.

Volatile Matter. One g. of the pigment is weighed in a platinum crucible closed by a well-fitting internal capsule lid, and the covered crucible, placed on a support of platinum or nichrome wire, is heated for seven minutes at a temperature of 900°-950°, cooled, and weighed. The loss in weight represents the volatile matter, including moisture in the air-dried sample. Duplicate results should not differ by more than 0·5 per cent.

Lamp and gas blacks may contain small traces of sulphur and free sulphuric acid. Should a complete analysis of these be necessary, reference should be made to the methods described in the above-mentioned report, or to Fox and Bowles', *The Analysis of Pigments, Paints, and Varnishes*, p. 119.

For the estimation of carbon and insoluble mineral material, the following method is laid down in the American Circular of the Bureau of Standards, No. 94.

Carbon and Insoluble Mineral Material. One g. of the pigment is weighed in a porcelain dish, moistened with a few drops of alcohol and 20 c.c. of concentrated hydrochloric acid, covered and digested on a steam bath for fifteen minutes. The cover is removed and the contents of the crucible evaporated to dryness, moistened with hydrochloric acid followed by 25 c.c. of distilled water, filtered on a weighed Gooch crucible, and the residue washed with hot water until the washings are free from lead and iron. The crucible and contents are dried at 105°-110° for two hours and ignited for seven minutes in a current of dry carbon dioxide (using a Rose crucible cover) with a flame about 20 cm. high. After cooling in a current of dry carbon dioxide the crucible is weighed and then ignited with free access of air (or in a current of oxygen) until all carbon is consumed, cooled, and reweighed. The loss in weight is calculated as carbon and the final residue as insoluble mineral material. Lead and iron in the filtrate are determined by the usual methods.

Black Oxide of Iron. The analysis of this material may be carried out by the methods given under iron oxide pigments (p. 495), the proportion of iron being calculated to Fe_3O_4.

Black Oxide of Manganese. The analysis of manganese dioxide is best determined by distilling the pigment with hydrochloric acid and passing the evolved chlorine into a solution of potassium iodide,

the liberated iodine being titrated with standard *N*/10 thiosulphate solution. Manganese may be determined by any of the usual methods (see p. 471).

XI. Bronze Pigments.[1]

This name is applied to certain powdery substances possessing a metallic lustre and consisting of metallic alloys or compositions such as "Mosaic gold" (stannic sulphide). They are used for coating metallic or other objects, for the purpose of imparting to them a semi-dull metallic lustre. They are employed in the graphic industries, in the wallpaper and paper industry, and for various other purposes.

Bavarian bronze pigments have been shown to contain the following amounts of copper:—Copper red, 98·92 per cent.; purple, 98·82 per cent.; orange, 95·30 per cent.; pale bronze-yellow, 82·34 per cent.; and intense yellow, 81·55 per cent. The analysis is carried out in the same way as that of a copper alloy containing zinc (*cf.* p. 220).

Besides the genuine bronzes, substitutes are also used, the oldest of which is "Mosaic gold" (stannic sulphide). They are employed more especially in cases where genuine bronzes would be injured by acid fumes and hydrogen sulphide.

Tungsten Bronze (Sodium para-tungstate) has been suggested as a substitute for bronze pigments; it possesses a magnificent golden yellow colour; the corresponding potassium salt is purple and in sunlight has a copper-like lustre; the lithium salt has the colour of blue-tempered steel. These substitutes have not, however, as good covering power as the bronze pigments, for, unlike the latter, they do not possess the characteristic cleavage into lamellæ necessary for intense reflection of the coloured rays of light.[2]

XII. Lakes from Artificial Dyes.[3]

Lakes are pigment colours which are produced by converting soluble dyes into insoluble compounds. They differ, as regards preparation and composition, from naturally occurring products, such as ochre, umber, etc., and from those which are obtained by the chemical decomposition of salts—*e.g.*, lead chromate, Prussian blue, etc.

[1] *Cf.* C. Hebing, *Vergoldung und Bronzierung;* G. Buchner, *Die Metallfärbung*, p. 194; L. E. Andrés, *Blattmetalle, Bronzen und Metallpulver.*

[2] *Cf.* A. W. Hofmann, *Reports of the Juries of the International Exhibition*, London, 1863, p. 83.

[3] W. Allsebrook, *J. Oil and Col. Chem. Assoc.*, 1919, 2, 125; J. B. Shaw, *ibid.*, 1920, 3, 57; F. H. Jennison, *ibid.*, 1922, 5, 145. Cf. *The Manufacture of Lake Pigments from Artificial Colours*, by F. H. Jennison, 2nd Ed., 1920.

Lake Precipitants for Acid Dyes. The substances most largely employed are:—Barium chloride, lead nitrate or acetate, zinc sulphate, aluminium sulphate or acetate, alum, stannous chloride, antimony pentachloride, calcium nitrate or acetate, sodium acetate and phosphate.

Lake Precipitants for Basic Dyes. These comprise:—Tannic, phosphoric, arsenious, antimonious, stannic, tungstic acids, rosin and palmitic, and stearic acids.

Lake Bases (Substrata). These are chiefly: Barium sulphate, as barytes (natural) and blanc fixe (precipitated $BaSO_4$), clay, China clay, calcium sulphate, kieselguhr, red lead, zinc oxide, lead sulphate, aluminium hydroxide, calcium carbonate, aluminium phosphate, aluminium arsenite, barium phosphate, lead carbonate, calcium phosphate, lamp black, lithopone, orange lead, green and white earth.

Examination of the Colouring Materials.—A small quantity of the colour is mixed with glue water or gum, spread on paper, and dried at 40°-50°; the specimen is then compared with standard colours. The surface, which is tested by the feel, and the depth and richness of colour are also examined; these properties, together with the results of examination of the base, often afford hints as to the method of preparation of the lake.

Part of the coloured paper is heated at 100°, in order to observe if the shade changes or if the colour is otherwise affected at this temperature.

Separate pieces of the paper are treated with a drop of 10 per cent. and with stronger nitric and hydrochloric acid and with concentrated and dilute sodium or potassium hydroxide, and the results are referred to tables of dye tests in order to identify the dye.[1]

The pigment may also be rubbed out with a little oil on a glass plate and the shade and undertone noted. It may be reduced with ten or twenty times its weight of zinc white, and if the pigment gives the same shade in oil and on reduction as one of standard or known pigments, it is probably identical with it. Fastness to *bleeding* and fastness to *light* must be determined. If the pigment is for use as a pulp colour it may be rubbed out on paper in size; if as an oil colour, it may be painted out on some surface and allowed to dry. A white in size is painted over the dry film in the case of a pulp, or a white in various media, *e.g.*, gold size, or some vehicle reduced with turpentine, white spirit, alcohol, or ether, in which the colouring matter is soluble, whereby bleeding of the colour into the white will be observed.

If sunlight is not available the films of the pigment may be exposed to the rays of a violet carbon arc with a filter of thin Vita-glass between the pattern and the arc.[2]

[1] *Cf.* the section on "Organic Dyes," Vol. IV. [2] S. G. Barker, *Chemical Age*, 1927, 17, 368.

Ordinary *Yellow Lakes* are prepared from naphthol yellow S, auramine, thioflavine T, quinoline yellow, and metanil yellow. Comparative tests with standard samples usually serve as a rapid means for recognition of the dye. The acid test is also of assistance in the identification.

Naphthol Yellow S. On treatment with hydrochloric acid the colour disappears almost completely. With nitric acid it first becomes reddish but decolorisation soon follows.

Metanil Yellow. Hydrochloric acid turns the colour much redder; with nitric acid it turns nearly scarlet.

Auramine O. Both nitric and hydrochloric acid cause almost complete decolorisation.

Quinoline Yellow. Hydrochloric acid produces scarcely any change; with nitric acid it becomes redder.

Thioflavine T. Nitric and hydrochloric acids cause decolorisation. With sodium hydroxide it turns redder (auramine is decolorised).

The *Orange Lakes*, almost without exception, are prepared from azo-dyes. The lakes made from Mandarin, R and G, and Orange II (Basle) are inferior to the brilliant Oranges, O and R, of Meister Lucius and Brüning. Very often mixtures are used of a cheap dye to give richness and depth, and a more expensive one to give increased brilliancy and stability. The behaviour of these dyes towards reagents is practically the same; the examination rests essentially on comparison with standards. The comparative effect of light during a period of two to three days is a useful test in this case.

Greater difficulties occur in the examination of *Red*, *Scarlet*, and *Crimson Lakes*. The following may be employed for their preparation:—Eosins, alizarin, and azo-dyes, and basic dyes such as safranine, fuchsine, rhodamine, methyl violet, etc.

Eosine Lakes are, after short experience, easily recognised by their vividness, depth of colour, and want of permanence to light. Even after two or three hours' exposure incipient fading may be observed. The identification of a particular eosin is not easy, because all eosin lakes are toned by the addition of various basic colours to give the required shade. Treated with acid they become yellow; with alkali the dye is separated from the base; addition of alcohol usually produces a fluorescent solution.

Alizarine Lakes are also coloured yellow by acids, but more slowly. Alkalis cause no change.

Fast or Permanent Reds (*e.g.*, Helio Fast Red) show but little change when treated with dilute acids or dilute alkalies. This, together with their fastness to light, which is superior to that of all but alizarine lakes, gives a ready means of identifying them.

The monoazo dye derived from *m*-xylidine sulphonic acid and R salt gives with lake-forming metallic bases yellowish scarlet lakes of remarkable fastness to light.[1]

Pure *Fuchsine*, *Rhodamine* and *Safranine Lakes* are easily identified by their characteristic shades; greater difficulties in identification arise when mixtures of dyes are present.

Violet Lakes, rhodamine, fuchsine, etc., are employed for shading. Violet Lakes, with the exception of those derived from gallein which become brown with acids, are for the most part derived from methyl violet and acid treatment changes them to a blue colour.

Blue Lakes are obtained from the various blues, *e.g.*, Nile blue, methylene blue, Bâle blue, and New blue; also from Water blue, Alkali blue, etc. Blues derived from alizarin colours are uncommon, while the erioglaucines and dyes of similar constitution are extremely sensitive to acids and alkalis. These dyes are recognised by the reactions given in the section on "Organic Dyes," Vol. IV.

Brown Lakes are mostly prepared from Bismark brown toned down with other dyes. The acid browns are used to some extent, but the difference in the lakes produced is great and they are easily recognised as acid colours.

Green Lakes contain dyes of the triphenylmethane series which are either basic or sulphonated amido-colours, the acid properties of which overcome the strong basicity of the amido groups, but from which lakes can be formed only when amido- and sulphonic-acid groups have entered into combination. Many basic greens (malachite green) combine with green earth directly giving shades fast to light, alkalis and non-bleeding. The quality of the green earth is of as much importance as that of the green dyestuff.

Black Lakes possessing a rich, deep shade are difficult to prepare, and are little used.

Examination of the Substratum.—Admixtures of finely ground mineral substances may generally be detected by feel when the sample is rubbed on paper. For a general analysis a small portion of the dry lake is heated in a porcelain crucible. Arsenic trioxide can be recognised by the garlic-like odour of its vapours. If the residue, after ignition, dissolves almost completely in dilute hydrochloric acid, and, on addition of ammonia to the solution, a precipitate of aluminium hydroxide is formed, it is fairly certain that a lake precipitated on a base of aluminium arsenite is being dealt with. The presence of a phosphate may be proved by ammonium molybdate.

For a complete examination, the residue after ignition, the greater part of which is usually soluble in boiling hydrochloric acid, is submitted to qualitative analysis.

[1] E. P. 164053, 5th December 1919.

An insoluble residue usually consists of clay, barium sulphate, calcium sulphate, or mixtures of these substances.

When ochres or other highly ferruginous compounds have been used as part of the base, the colour of the ash and the quantity of iron present indicates their presence.

LITERATURE.

CHURCH, Sir A. H.—*The Chemistry of Paints and Painting*, 4th edition, 1915.
CHURCH, Sir A. H., and OSTWALD, W.—*Farben und Malerei*, 1908.
EIBNER, A.—*Malmaterialienkunde*, 1909.
FOX, J. J., and BOWLES, T. H.—*Analysis of Paints and Pigments*, 1926.
GARDNER, H. A., and SCHAEFFER, J. A.—*The Analysis of Paints and Painting Materials*, 1911.
GARDNER, H. A.—*Physical and Chemical Examination of Paints, Varnishes and Colors*, 1925.
GENTELE, J. G.—*Lehrbuch der Farbenfabrikation*, 3rd edition, 1906.
HOFFMANN, R.—*Ultramarin*, 1902.
HOLLEY, C. D. and LADD, E. F.—*Analysis of Mixed Paints, Colour Pigments and Varnishes*, 5th edition, 1908.
HURST, G. H.—*A Manual of Painters' Colours, Oils and Varnishes*, 5th edition, 1913.
JENNISON, F. H.—*The Manufacture of Lake Pigments from Artificial Colours*, 2nd edition, 1920.
JONES, M. W.—*The Testing and Valuation of Raw Materials used in Paint and Colour Manufacture*, 1900.
LAURIE, A. P.—*The Painter's Methods and Materials*, 1926.
MIERZINSKI, A.—*Handbuch der Farbenfabrikation*, 1898.
MORRELL, R. S., and DE WAELE, A.—*Rubber, Resins, Paints and Varnishes*, 1921.
PARRY, E. J., and COSTE, J. H.—*The Chemistry of Pigments*, 1902.
SABIN, A. H.—*White Lead, its Use in Paint*, 1920.
SABIN, A. H.—*Red Lead and how to use it in Paint*, 3rd edition, 1920.
SCOTT, W. W.—*Standard Methods of Chemical Analysis*, 4th edition, 1925.
SOURIS, A.—*Le Blanc de Zinc et le Lithopone*, 1912.
ZERR, G.—*Tests for Coal-tar Colours in Aniline Lakes*, translated by C. Mayer, 1910.
ZERR, G., and RÜBENCAMP, R.—*A Treatise on Colour Manufacture*, translated by C. Mayer, 1908.

PAINT VEHICLES, JAPANS AND VARNISHES

By R. S. MORRELL, M.A., Ph.D., F.I.C. (Messrs Mander Bros., Wolverhampton).

General Considerations for the Examination of Paint Vehicles.

THE vehicle or liquid portion of a paint may contain drying oils, turpentine, mineral oil distillates, alcohols, ketones, volatile esters, resin and cellulose varnishes, oil varnishes, driers, and even water. In the examination of a paint the uniformity of the sample must be assured, and the volume as well as the weight must be determined. The separation of the vehicle from the pigment, although apparently simple, requires careful consideration, and in the extraction of the vehicle the choice of solvents is of importance. When 90 per cent. benzene is not available, petroleum spirit (boiling-point below 60°) may be used, but if varnish resins are present it cannot be employed, because they are incompletely soluble in this solvent. If the paint contains water, acetone is a suitable solvent.

Mixtures of 50 per cent. benzene, 30 per cent. wood alcohol, and 20 per cent. refined acetone or of 10 vols. methylated ether, 6 vols. benzene, 4 vols. methyl alcohol, and 1 vol. of acetone, finishing the extraction with methylated ether, have been found to be convenient solvents. The extraction of the vehicle may be carried out in an apparatus of the Soxhlet pattern, and the residue (pigment) dried and weighed; but this process is rather slow and does not give always satisfactory results. If the viscosity of the paint is reduced by warming it for twenty-four hours in a tall cylinder, the oil vehicle may frequently be removed. The most convenient method is to centrifuge the paint at 70° in tightly corked cylinders, whereby a rapid separation of the pigment is obtained. Final centrifuging with petroleum spirit will remove the last traces of linseed oil and leave the pigment dry. It is advisable to avoid oxidation during the process, and instead of petroleum spirit, methylated ether may be employed. It must be remembered that no method of extraction will give accurate results, because the last traces of oil cannot be removed owing to the formation of soaps by the metallic oxides of the pigment.

There are some pigments which by their low specific gravity, colloidal nature or partial solubility cannot be completely separated from oil by settling, extraction or centrifuging, *e.g.*, lampblack and other forms of carbon, zinc oxide, and Prussian blue. When colloidal pigments, *e.g.* zinc oxide, are present in a paint they may be separated by adding to the paint three or four times its volume of fuller's earth, diluting the mixture with light petroleum and centrifuging, whereby the fuller's earth carries down the colloidal pigments. Where lampblack and Prussian blue are present in paste colours the Prussian blue can be determined by the Kjeldhal-Gunning method; the nitrogen found is multiplied by 4·4 to give the amount of Prussian blue. For the determination of lampblack, a portion of the paint may be boiled with excess of alcoholic potash until all the oil is saponified. The mixture is decanted through a filter and washed first with hot alcohol and then with hot water, whereby a good separation of the vehicle from the pigment is afforded. By this method any Prussian blue present is partially destroyed and part of its iron content remains with the black pigment on the paper.[1]

Fox and Bowles[2] recommend the use of petroleum spirit boiling below 60°. Ten to fifteen g. of the paint are extracted with about 100 c.c. of the spirit. Generally four extractions are sufficient, and the pigment is left in such a condition that it can readily be broken up into a fine powder by means of a glass rod.

When the paint contains varnish gums, the extraction with petroleum spirit is not complete, and it is advisable to use the mixture recommended in the United States Government Specification for paints, viz., ethyl ether 10 vols., benzene 6 vols., methyl alcohol 4 vols., and acetone 1 vol.

A rapid method of estimation of the vehicle from the settled paint in the can may be carried out by heating a weighed portion in a tared flask fitted with a Liebig's condenser. Heating to 180° will drive off nearly all the volatile constituents. A portion of the residue in the flask, which consists of oils, driers, and resins may be transferred to a crucible and ignited, while the residue may be weighed and analysed for driers. Another portion of the original vehicle removed from the paint may be evaporated in a stream of carbon dioxide or in vacuo below 150°, whereby the oil is left in the residue.

A more general method is to remove the volatile component by distillation with steam. The distillate is received in a suitable separating funnel and the aqueous layer is run off from the bottom as the distillation proceeds. The aqueous layer should be kept to be examined for thinners soluble in water. When thinners contain hydrocarbons boiling over 200°, prolonged distillation will be required

[1] W. W. Scott, *Standard Methods of Chemical Analysis*, 1917, p. 611.

[2] *Analysis of Pigments and Varnishes*, 1927, p. 129.

to recover all the volatile matter. Holley uses steam distillation at 130°-135° and adds about 75 g. of paraffin wax (m.p. 125°-130° F.) to the flask in order to keep the mass in a freely fluid condition during the entire volatilisation of the thinner. The quantity of volatile thinners in a mixed paint may range from 3 or 4 per cent. in a simple linseed oil paint to 30 or 40 per cent. in a gloss paint.

Colophony due to resinate driers can be detected in the petroleum spirit extract of the paint by the Liebermann-Storch reaction, but its presence is not certain evidence of the use of metallic resinates. The reaction is carried out by dissolving the varnish in ether, extracting with soda, acidifying the soda solution and removing the separated rosin acids with ether. Acetic anhydride is added and the solution is poured into a flat basin. On the addition of a drop or two of sulphuric acid (1 : 1) a violet colour indicates rosin. If much resin is present the colour radiates from the point where the acid enters. The reaction is also given by ester gums, which invariably contain a small proportion of uncombined rosin. Wolff[1] recommends that the ether solution of the rosin be evaporated and the residue dissolved in ten times its bulk of petroleum spirit. Three or four drops of this solution are used for the sulphuric acid test. The addition of ammonia to the rest of the petroleum spirit solution will cause gelatinisation if rosin is present. The approximate percentage of rosin can be determined by extraction with 97 per cent. alcohol.

A rapid method of estimation of oil in paint, if rosin is absent and the amount of the thinners is small, may be carried out as follows:—25 g. of the paste paint is saponified on a water-bath for half an hour with 15 c.c. of sodium hydroxide (100 g. in 300 c.c. of water) and 75 c.c. of alcohol. After addition of 100 c.c. of water, boiling with excess of sulphuric acid (8 to 10 c.c., sp. gr. 1·2) and removal of the solid pigment, the liberated oil acids are extracted with 50 c.c. methylated ether and with water, and after washing the ethereal solution and drying it over anhydrous sodium sulphate the oil acids can be examined after evaporation of the ether.

Determination of Water in Paints. For the separate estimation of water present in a paint, the method recommended in the British Standard Specifications for ready mixed linseed oil paints issued by the British Engineering Standards Association may be followed[2]:—

One hundred g. of paint shall be weighed in the flask (see Fig. 51), 100 c.c. of petroleum spirit (boiling between 80° and 100°) and 1 c.c. of dry amyl or ethyl acetate added, and the contents of the flask well mixed. Petroleum spirit

[1] *J. Soc. Chem. Ind.*, 1914, 33, 363.

[2] Abstracted by permission of the British Engineering Standards Association, from B.S. specification No. 261, official copies of which can be obtained from the Secretary, 28 Victoria Street, S.W. 1, price 2s. 2d. post free.

shall be poured into the receiver up to the level of the side tube. After connecting the flask to the apparatus, the oil bath, which should contain sufficient heavy mineral oil to cover the flask nearly to the neck, shall be heated to such a temperature as to keep the contents of the flask boiling briskly. Distillation shall be continued until no further water collects in the receiver. At the

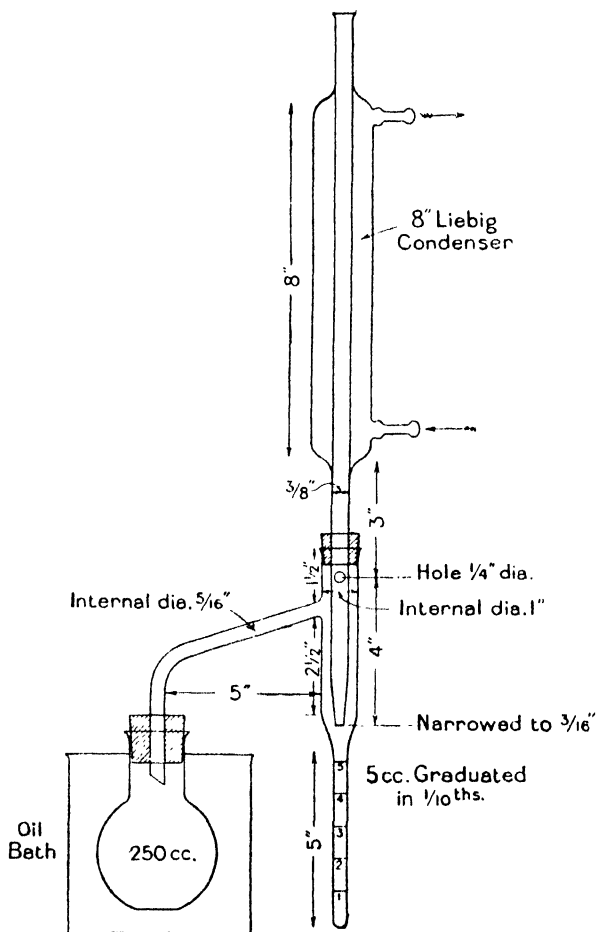



Fig. 51.

conclusion of the determination any water still clinging to the condenser tube can be released and caused to fall into the receiver by pushing a wire or a small camel hair brush attached to a glass rod through the condenser tube from the top, and any condensed water on the sides of the receiver shall be dislodged after dismantling the top part of the apparatus.

Note.—It is important that the receiver and condenser should be thoroughly clean. They should, therefore, be treated with a mixed solution of potassium

dichromate and sulphuric acid or other suitable cleansing agent prior to the determination. When the apparatus is in constant use it is usually sufficient to clean it after every third estimation.

The most important media for oil paints and enamels are a vegetable drying oil and turpentine or turpentine substitute with or without a resin. The chief components of oil varnishes are a vegetable drying oil and a thinner, which may be turpentine or a turpentine substitute, together with a resin or, in black enamels, a bitumen or carbon black. In distempers the pigment is held by a size binder, or in water paints by a binder composed of gelatin or casein forming a stable emulsion in water with a drying oil.

In spirit varnishes the resin or the solid component of the film, which may be a soluble cellulose, is dissolved in a variety of vehicles of which ethyl alcohol is generally the main component thus giving the name spirit varnish to this special class. For the classification of varnishes reference may be made to text-books dealing with the subject.[1]

The most important component of paints and varnishes generally is a drying oil of which linseed and China wood oils are the most popular. Other drying oils, such as walnut, poppy, hemp, and niger, perilla and menhaden are used only for special purposes; the two first are used in artists' colours and are not met with in commercial paints and varnishes.

The Examination of Drying Oils.

The oil extracted from the paint may contain varnish resins, unless the paint is only an oil paint. If a special examination of the oil medium is required it is preferable to use the fatty acids obtained from the oil since they can be procured reasonably free from varnish resins. Fox and Bowles[2] recommend the following procedure:—50 g. of the paint is stirred in a beaker with 250 c.c. of petroleum spirit and allowed to settle. The supernatant liquid is decanted into a flask and further extractions are made until all soluble matter has been removed. If the first extraction is made with a large excess of petroleum spirit much of the varnish resin dissolved will separate out on cooling the solution with ice. The petroleum spirit is distilled off on a water bath in a current of dry carbon dioxide or nitrogen. Fifteen c.c. of a strong solution of sodium hydroxide (sp. gr. 1·3) and

[1] F. Seeligman u. E. Zieke, *Handbuch der Lack- und Firnisindustrie*, 3te Auflage, 1922; Ch. Coffignier, *Les Vernis*, 1921; A. H. Sabin, *Technology of Paint and Varnish*, 1917; R. S. Morrell, *Varnishes and their Components*, 1923; F. Sproxton, *Cellulose Ester Varnishes*, 1925; T. H. Barry, A. A. Drummond, and R. S. Morrell, *Natural and Synthetic Resins*, 1926; J. J. Fox and T. H. Bowles, *The Analysis of Pigments, Paints and Varnishes*, 1927; S. P. Wilson, *Pyroxytin Enamels and Lacquers*, 1926.

[2] *loc. cit.*

75 c.c. of methylated spirit are added to the residue and the mixture is heated for one hour under a reflux condenser until saponification is complete. The bulk of the alcohol is distilled off in a current of an inert gas; water is added, and the distillation continued until no more volatile thinners pass over. The contents of the flask are diluted with distilled water and transferred to a separating funnel. If adulteration with mineral oil is suspected, it must be extracted from the soap at this stage with petroleum spirit, and the oily layer separated, washed with water and evaporated in a tared flask or beaker and weighed. The soap solution to which the washings from petroleum ether have been added is acidified with hydrochloric acid and 50 c.c. of petroleum spirit added. The petroleum spirit solution may contain suspended matter consisting of oxidation products of the fatty acids and resin, as well as insoluble varnish products. The filtered and water-washed petroleum solution of the fatty acids is evaporated down in a current of carbon dioxide. The fatty acids thus obtained will be sufficiently pure for the identification tests for the drying oils described below, unless appreciable quantities of rosin are present in the paint. In this case the separation of the rosin from the fatty acids must be effected by Twitchell's method, which is described under the analysis of varnishes (p. 604).

In the examination of a drying oil it may be advisable to determine (1) specific gravity; (2) iodine value; (3) acid value; (4) saponification value; (5) unsaponifiable matter; (6) moisture; (7) the percentage of oxidised acids; (8) the refractive index; (9) the ether-insoluble bromide value of the oil or of its corresponding acid; (10) the drying time of the oil against a standard linseed oil; (11) mucilage; (12) the colour; (13) the viscosity. Nos. 1, 2, 3, 4, 9, 10, and 11 are generally essential. The determination of the refractive index of China wood oil (1·5180 at 20°) is of importance.

Specific Gravity. (*Cf.* Vol. I., pp. 116-134.) Either a specific gravity bottle or a Sprengel tube may be used, but generally the Westphal balance is preferred, especially when considerable quantities of the oil under examination are available and it is not too viscous. With the exception of China wood oil (sp. gr. 0·940 at 15°·5), all the drying oils have specific gravities lying between 0·925 and 0·933. Bodied oils, which have been produced by the action of heat, have specific gravities increasing with viscosity up to 0·9912 (15°·5).

Iodine Value. The most important methods for the determination of this value are the Hübl[1] method with modifications proposed Waller,[2] and Wijs,[3] and Hanus.[4]

[1] *J. Soc. Chem. Ind.*, 1884, p. 641.
[2] *Analyst*, 1890, **15**, 56. [3] *Ibid.*, 1900, **25**, 33.
[4] *Z. Unters. Nahr. u. Genussm.*, 1901, 1913.

The Hübl method requires the following solutions:—(*a*) an iodine solution, which is prepared by dissolving 25 g. of iodine in 500 c.c. of 95 per cent. alcohol, is mixed with 30 g. of mercuric chloride dissolved in 500 c.c. of 95 per cent. alcohol. These solutions should be mixed as required and the mixture be allowed to stand twenty-four hours before use; (*b*) a standard solution of sodium thiosulphate and a solution of potassium iodide free from iodate. The solvent for the oil is generally chloroform or carbon tetrachloride, which should be pure. Ether must not be used, but benzene (free from thiophene) or glacial acetic acid may be employed.

The determination of the iodine value is carried out as follows: 0·15 to 0·18 g. drying oil (0·2 to 0·3 g. semi-drying oil) is weighed accurately into a bottle of 500-800 c.c. capacity, provided with a well-ground stopper. The oil is dissolved in 10 c.c. chloroform or carbon tetrachloride, and 25 c.c. iodine solution run in from a pipette. In order to prevent loss of iodine by volatilisation it is advisable to moisten the stopper with potassium iodide solution. The solvent and the iodine solution must give a clear mixture, otherwise more solvent must be added. The mixture must exhibit a dark brown colour after twelve to eighteen hours in the case of drying oils, otherwise 25 c.c. more of the iodine solution must be added, and the mixture well shaken and diluted with 400 c.c. water. If a red precipitate of mercuric iodide appears, more potassium iodide must be added. Standard thiosulphate is run in until both water and solvent layers are only slightly coloured; starch solution is added, and the titration finished in the usual manner. Immediately before or after the titration with thiosulphate, 25 c.c. of the original iodine mercuric chloride solution is standardised in the same manner so as to form a control experiment. The difference between the amounts of iodine found, calculated in terms of iodine to units per cent. of the sample, will give the iodine value.

The scheme of the Hübl reaction may be expressed as follows:—

$$HgCl_2 + I_2 = HgClI + ICl$$
$$HgClI + I_2 = HgI_2 + ICl.$$

The reaction, which is incomplete and reversible, is best represented by the equations given above. In the presence of water the following reactions may occur simultaneously:—

$$ICl + H_2O = HCl + HIO$$
$$5HIO = HIO_3 + 2H_2O + 4I$$
$$HIO_3 + 4I + 5HCl = 5ICl + 3H_2O.$$

Of the reaction products, HIO and HIO_3 will react in the presence of hydrochloric acid to give iodine.

In Waller's modification the hydrochloric acid used inhibits the reaction represented by the first of the second series of equations and prevents the formation of hypoiodous acid, which would oxidise the alcohol and so disturb the equilibrium.

In Wijs's modification[1] the iodine solution consists of iodine trichloride and iodine in the proportions to give iodine monochloride, which are dissolved separately in glacial acetic acid, or the iodine monochloride is prepared by passing dry chlorine into iodine dissolved in good glacial acetic acid. The Wijs solution is allowed to react with the drying oil in the same manner as the Hübl, but for a much shorter time; half an hour to six hours may be required according to the unsaturation of the glyceride.

If acetic acid reacts with the oil under examination the Hübl solution must be used. The Hanus modification contains iodine bromide and is considered by American chemists to be superior to the Wijs solution, and its use is recommended in American standard specifications of linseed oil.

The principle of the Wijs or Hanus method is simple :—

$$\underset{(Br)}{ICl} + \;\rangle C = C \langle \;\longrightarrow\; \rangle \underset{I}{C} - \underset{Cl(Br)}{C} \langle$$

Sundberg and Lundborg[2] state that the Hanus method gives results with fats which agree closely with those found by the Hübl method; Wijs's method gives higher results. In linoleic acid (linoleic acid is the name given to a mixture of oleic, linolic, and linolinic acids obtained from linseed oil) the Hübl value lies nearer to the theoretical than the Wijs value.[3] Marshall proposes the use of carbon tetrachloride, and Aschmann prepares a solution of iodine trichloride in water by passing chlorine into potassium iodide solution until the iodine liberated is dissolved; after filtering from potassium iodate the solution is allowed to react with a chloroform solution of the oil or fat for twenty-four hours. The values obtained lie between those obtained with the Wijs and Hübl solution. Kelber and Rheinheimer[4] and P. Gillot[5] prefer Wijs's method because of the greater stability of the solution and the rapidity of the process. MacLean and Thomas[6] have investigated the behaviour of sterols (*e.g.* cholesterol) with the Hübl and Wijs reagents; with sterols the Hübl solution gave values approximating to those required by the

[1] P. J. Fryer and F. E. Weston, *Technical Handbook of Oils, Fats, and Waxes*, **2**, 92.
[2] *Analyst*, 1920, **45**, 338.
[3] *J. Soc. Chem. Ind.*, 1900, **19**, 213.
[4] *Ibid.*, 1918, **37**, 34A.
[5] *Ann. Falsif.*, 1925, **18**, 335.
[6] *Biochem. J.*, 1921, **15**, 319.

number of double bonds believed to exist in the sterol molecule. With the Wijs reagent the results may be twice as high as those obtained with the Hübl solution, and vary greatly with the temperature, time of contact, and proportion of the reacting substances. The difference in behaviour of the two reagents appears when they react with the sterols (not with reduced sterols) and with the resinic acids, possibly also with the naphthenic acids, though in the latter definite substances of known constitution have not been investigated. The effect appears to be due to the influence of the glacial acetic used in the solution as solvent for the iodine trichloride, and affords evidence that a considerable amount of substitution takes place. The substitution effect is particularly noticeable when a condensed ring-nucleus containing one double bond reacts with Wijs's solution; thus abietic acid, containing two double bonds, and dihydroabietic acid, containing one double bond, give identical values with the Wijs solution, so that substitution must be much greater in the reduced derivative. Anthracene reacts similarly with Hübl and Wijs's solutions, giving high iodine values in both cases, but phenanthrene and retene (isopropyl-dimethylphenanthrene) are hardly affected by Hübl's solution, but absorb considerable amounts of iodine from Wijs's reagent. For drying oils the Wijs method may be recommended as most convenient, but in dealing with ring compounds the Hübl method is perhaps safer. Wijs's method gives accurate results with China wood oil, but two units lower than the Hübl method.[1]

The determination by Wijs's method is carried out as follows:— 0·16 to 0·18 g. of the oil is used for the determination with 25 c.c. of the Wijs solution. If a larger quantity of oil is taken the quantity of solution must be increased, because it is essential that an excess of iodine greater than that which has been absorbed shall be left at the end of the reaction. Ten c.c. of pure carbon tetrachloride is added to the bottle and when the oil is dissolved 25 c.c. of the Wijs's solution is introduced. The stopper of the bottle is moistened with potassium iodide solution and placed firmly in position. The bottle is placed in the dark for about three quarters of an hour at 60°-70° F. The stopper and the neck of the bottle are washed down with 15 c.c. of a 10 per cent. solution of potassium iodide, 100 c.c. of distilled water added, and the excess of iodine titrated with *N*/10 sodium thio-sulphate solution. Towards the end of the titration about 2 c.c. of starch solution is added, and the contents of the bottle are shaken vigorously after each addition of the thiosulphate solution, which is added until the contents of the bottle are colourless. The carbon tetrachloride used must not react with Wijs's solution and the potassium iodide must be free from iodates.

[1] H A. Gardner, *Proc. Amer. Soc. Test. Mats.*, 1922, **22**, I., 367.

The Wijs solution is made by either of the following alternative methods:—

Method 1. Eight g. of iodine trichloride shall be dissolved in approximately 400 c.c. of glacial acetic acid. 8·7 g. of iodine shall be dissolved in a further quantity of 450 c.c. of glacial acetic acid, the mixture being gently heated, if necessary, to effect solution. The two solutions shall then be mixed and made up to 1000 c.c. with glacial acetic acid.

Method 2. 12·7 g. of iodine shall be dissolved in 1 litre of glacial acetic acid, the mixture being gently heated, if necessary, to effect solution. The solution so obtained shall be cooled and the halogen content determined by titration of 10 c.c. with standard sodium thiosulphate solution. A stream of dry chlorine shall then be passed into the iodine solution until the halogen content as determined by subsequent titration has been doubled. (This is denoted by a change in colour of the solution from dark brown to clear orange.) It is of importance to warm the Wijs solution prepared by either of the methods for twenty minutes at 100° in order to stabilise it.

During the preparation of the solutions, access of water vapour shall be prevented. The acetic acid used shall contain not less than 99 per cent. of acetic acid, and a permanent pink coloration shall be produced when 0·2 c.c. of *N*/10 potassium permanganate solution is added to 5 c.c. of the acid.

Acid Value. The acid value may be expressed as the number of milligrams of potassium hydroxide required to neutralise 1 g. of oil. It is also stated as a percentage of free oleic acid in the oil, this acid being selected as a typical fatty acid occurring in vegetable oils. The acid value of a drying oil is a variable, depending on the quality of the sample and on the mode of extraction of the oil from the seed. Rancidity and oxidation both increase the acid value. For the determination of the acid value a mixture of 50 per cent. alcohol and benzene is used as the medium for the oil. It has been found that such a mixture gives a more reliable result than when alcohol alone is used. The acid values of some common oils are as follows:— Linseed oil, 1-2·5; China wood oil, 2·2-5; Soya oil, 0·1-1·25.

Saponification Value. The gross saponification or Köttstorfer value represents the amount of potassium hydroxide required to neutralise the free and combined acid constituents of a fat or oil, and is expressed in terms of parts of potassium hydroxide per 1000 parts of the fat or oil. The saponification value as determined by the usual method includes the alkali required for the neutralisation of any free acid in the oil, and the acidity must be subtracted from the Köttstorfer value to give the true saponification value.

The determination is carried out as follows:—1·5-2 g. of the sample is weighed into a flask of 150-200 c.c. capacity, and 25 c.c. of approximately *N*/2 alcoholic solution of potassium hydroxide is added. A long cooling tube is attached to the flask, which is then heated on a

boiling water bath for half an hour and occasionally shaken. It is then allowed to cool, phenolphthalein added, and the excess alkali titrated back with *N*/2 hydrochloric acid (not sulphuric). A blank test must be carried out at the same time.

The values for a few principal drying oils are as follows:—Linseed oil, 192·5; China wood oil, 193; Perilla oil, 189·6; Soya oil, 193; Para rubber-seed oil, 206; Poppy-seed oil, 195.

Unsaponifiable Matter. The unsaponifiable matter in fats and oils includes all substances which are insoluble in water, but soluble in the fat solvents specified below after alkali saponification of the fats and oils. It is taken to include alcohols (other than glycerine), *e.g.* sitosterol (phytosterol) in vegetable oils and cholesterol in animal oils and fats. Certain fish oils from the shark and dogfish families contain unsaponifiable hydrocarbons (squalene, spinacene, etc.) Some waxes yield insoluble alcohols on treatment with alkalis. The unsaponifiable matter generally remains dissolved in the soap solution after saponification. The principle of the method of estimation depends on the solubility of the unsaponifiable matter in ether or in petroleum ether, whereas the soaps are practically insoluble, whether they are in solution or in the dry state. It is better to use ether instead of petroleum ether, and to get rid of any soap, which may have been taken up into the ether by wax alcohols or hydrocarbons, by treatment with a little water and re-extraction with ether. For the experimental details reference may be made to the Report of the Committee of Analysts on the standard methods of analysis of seeds, nuts and kernels, fats, oils, and fatty residues (Ministry of Food, Oils and Fats Branch[1]); also to Boemer's method.[2] The amount of unsaponifiable matter in natural oils and fats is very variable, but in genuine samples it is quite small, *e.g.* linseed oil, raw or refined, and soya oil (crude or edible), each containing 1 per cent.

In the British Standard Specification for Linseed Oil (No. 243, 1926), the oil when tested in the following manner shall not contain more than 1½ per cent. of unsaponifiable matter[3]:—

"Five g. of the oil shall be boiled for one hour under a reflux condenser with 50 c.c. of alcohol containing 2 g. of sodium hydroxide (NaOH) in solution.

"The resulting soap solution shall then be transferred to a separating funnel with about 100 c.c. of hot distilled water and, after cooling, extracted successively with 100 c.c., 70 c.c. and 70 c.c., of redistilled ether.

---

[1] *Analyst*, 1920, 45, 278.

[2] Ubbelohde, *Handbuch der Oele u. Fette*, p. 261.

[3] Abstracted by permission of the British Engineering Standards Association, from B.S. specification No. 243, official copies of which can be obtained from the Secretary, 28 Victoria Street, S.W. 1, price 2s. 2d., post free.

"The ethereal extracts shall be mixed and washed as follows:—

"(*a*) Three times with successive quantities of 10 c.c. of a solution containing 1 g. NaOH in a mixture of 90 c.c. of water and 10 c.c. alcohol, and then

"(*b*) Five times with successive quantities of 10 c.c. distilled water.

"The ethereal solution shall be evaporated in a tared flask on a water bath. The flask and residue shall be heated in a hot water oven until the residue is free from water, and then shall be allowed to cool and weighed.

"In the event of the amount of unsaponifiable matter so determined exceeding the specified maximum, it shall be again boiled for half an hour with ½ g. of sodium hydroxide (NaOH) dissolved in 10 c.c. of alcohol.

"The unsaponifiable matter shall be extracted from the alkaline liquid in a similar manner to that described above, using proportionally smaller amounts of ether and water.

"The ethereal solution shall be evaporated and the residue reweighed.

"*Note.*—The accuracy of the estimation is increased if a counterpoise, consisting of a flask of similar size and shape, and made of the same glass, is used in determining the weight of the flask containing the unsaponifiable matter."

Moisture. The amount of moisture contained in a drying oil is variable, depending on its age and period of tanking. A good linseed oil should not contain more than 0·25 per cent. of moisture. The method of determination of the moisture is given in the Report of the Committee of Analysts mentioned on p. 573. A current of hydrogen is passed over asbestos saturated with the oil under examination, and the moisture is absorbed by concentrated sulphuric acid. In the opinion of the Committee this method is applicable to all fats and oils, to readily oxidisable oils like linseed oil, and to oils containing high percentages of free fatty acids of low molecular weight. It is doubtful whether the whole of the moisture is removed by the above method when the oil contains much mucilage. In fats and oils, which are free from uncombined fatty acids and are not readily oxidisable, the ordinary methods of drying on sand in a water oven may often be used.

Oxidised Fatty Acids. Drying oils become viscous on exposure to air owing to the formation of oxidised glycerides, and blown oils contain the same oxidation products. Their formation is accompanied by a reduction in the iodine value of the original oil. The estimation of the oxidised glycerides produced on the drying of paint or varnish is of importance. Fahrion[1] estimates the amount of oxidised acids in the following manner: 4 to 5 g. of the sample is saponified with alcoholic potash; the alcohol is evaporated off, the soap is dissolved in hot water, transferred to a separating funnel and decomposed with hydrochloric acid. After cooling, the liquid is shaken with petroleum

[1] *Z. angew. Chem.*, 1898, 782; 1903, 79; 1904, 1199.

ether (boiling-point below 80°) and is allowed to stand until it has completely separated into two layers. The insoluble oxidised fatty acids will be found to adhere to the sides of the funnel or to form a sediment in the petroleum ether layer. The aqueous layer is drawn off, the petroleum ether removed, if necessary, through a filter, and the oxidised acids washed with more petroleum ether to remove adhering fatty acids. If the amount of oxidised fatty acids is large, it is advisable to dissolve them in alkali, decompose the resulting soap with hydrochloric acid and shake out again with petroleum ether to remove any soluble fatty acids. The oxidised acids are then dissolved in warm alcohol or ether, the solution evaporated in a tared dish, and the residue weighed. Linseed oil blown for ten hours at 120° will contain 7·1 per cent. oxidised acids. Linseed oil blown with oxygen until its iodine value is 58·8 contains 42·82 per cent. oxidised acids. G. S. Petroff and A. T. Danilowitsch[1] state that weakly oxidised oils may give correct results with Fahrion's method, but highly oxidised oils give results which are too high, and to obtain correct results solution of the oxidised acids in alcohol must precede the petroleum ether extraction.

Refractive Indices of Drying Oils. (*Cf.* Vol. I., pp. 188-198.) The ease with which the refractive index can be determined makes the refractometer of importance in the examination of drying oils and varnish thinners. The refractive index does not give a perfectly reliable means of detecting adulteration, but in conjunction with other tests it serves to indicate whether a sample is genuine or not. For the use of the refractometer in the analysis of oils and fats, reference must be made to a paper by J. N. Goldsmith.[2] The refractive indices of oils decrease with rise in temperature, and the mean temperature correction per degree centigrade is 0·00036 (A. F. Joseph).[3] It is customary to determine the refractive indices of fluid drying oils at 20°. The refractive index of Indian linseed oil at 20° is 1·4710. The difference in the refractive indices of raw oil and boiled oil is comparatively small. Polymerisation of linseed oil is accompanied by a marked rise in the refractive index. Linseed oil thickened at 260-280° in carbon dioxide (sp. gr. 0·969) has a refractive index 1·49. Oxidation of the oil is accompanied by a rise in the refractive index. The refractive index of China wood oil (1·5172) is considerably higher than that of linseed oil, and this serves to detect adulteration as the value of the refractive index is lowered. The difference between the figures for China wood oil and soya oil at 40° being 0·0402, the addition of 10 per cent. or even 5 per cent. soya oil can be detected. More

[1] *Z. deutsch. Oel-Fett. Ind.*, 1925, 45, 668.
[2] *J. Oil and Col. Chem. Assoc.*, 1921, 4, 58.
[3] *J. Soc. Chem. Ind.*, 1920, 39, 661.

importance is attached in England to the determination of the refractive index of China wood oil as a test of purity than to the test of coagulation by heat. Instead of measuring the refractive indices of oils it is sometimes preferable to determine the refractive indices of the corresponding acids.[1]

In the examination of varnish thinners the refractometer is of use in analysing a large number of binary solvent mixtures: thus the percentage of white spirit in a mixture of turpentine and white spirit can be determined with fair accuracy from the value of the refractive index, because the relationship is expressed by a linear graph. It must be pointed out that the method is invalid when benzene is a component of the white spirit.

Hexabromide Test for Linseed and Other Oils. When treated under proper conditions with bromine, the unsaturated oils or acids absorb two atoms of the halogen for each unsaturated linkage. The solubility of the bromo-derivatives in ether decreases with increased bromine content, so that the hexa- and octobromides are only very sparingly soluble, whereas the di- and tetrabromo-derivatives are soluble. The fatty acids are generally used, because the glyceryl esters do not give concordant results. Many investigators have examined the conditions under which bromine is absorbed by unsaturated oils and acids. Hehner and Mitchell[2] have investigated the combination with glycerides, Eibner[3] and Muggenthaler[4] the compounds formed with fatty acids. Eibner's method has been slightly modified by G. W. Thompson.[5] Bailey and Baldsiefen[6] have examined the published methods for the hexabromide value, and find that the results obtained were not concordant. They recommend precautions in the preparation of the fatty acids and of the hexabromide, and suggest the following method :—

(a) *Preparation of Fatty Acids.* Approximately 50 g. of oil is weighed into a 2 litre round-bottomed flask, and 40 c.c. of caustic soda solution (sp. gr. 1·4) and 40 c.c. of alcohol added. The mixture is heated on a steam-bath for about half an hour. One litre of hot distilled water is added and the soap solution boiled, either over a free flame or on a steam-bath, to remove the alcohol, a stream of carbon dioxide being passed through the apparatus all the while. The solution is then cooled slightly and acidified with dilute hydrochloric acid (1 : 1). The mixture is warmed until the fatty acids form a clear layer, the current of carbon dioxide being continued. The fatty acids

[1] For details of the determination of the dispersion and dispersive power of an oil (n_F, n_C and n_D for F, C and D lines), see Fryer and Weston's *Oils, Fats, and Waxes*, Vol. II., p. 58.

[2] *Analyst*, 1898, p. 313.

[3] *Farben- Zeit.*, 1912, **18**, 131.

[4] *Inaug. Dissert.*, 1912, Augsburg.

[5] *Proc. Amer. Soc. Test. Mats.*, 1917, **15**, 233.

[6] *Ind. Eng. Chem.*, 1920, **12**, 1100.

are separated from the aqueous layer in a separating funnel and washed thoroughly with hot distilled water until the washings are neutral to methyl orange. The warm fatty acids are freed from water by centrifuging, and kept in a well-stoppered bottle.

(b) *Preparation of the Hexabromides.* One g. of fatty acids is accurately weighed into a weighed centrifuge tube (1 in. diameter and 5 in. long) and dissolved in 25 c.c. of specially prepared ether (Methylated ether is washed with 10 per cent. of its volume of ice-cold distilled water. After separating the water and repeating the washing three times, the washed ether is dried over fused calcium chloride and the drying completed by sodium. After distillation the ether is treated with an excess of finely powdered hexabromide of the fatty acids of linseed oil previously prepared. The ether solution, kept at least for three hours at 0°, is decanted into a dry bottle.)

Bromine solution (5 c.c. bromine in 25 c.c. glacial acetic acid made up just before use) is added very slowly to the fatty acids dissolved in ether until a deep red colour is produced. The tube is then allowed to stand in an ice-chest overnight. The solution is separated from the precipitate by centrifuging, and the precipitate repeatedly washed with the specially prepared ether and the last traces of the ether removed in a vacuum. The precipitate is then weighed.

Steele and Washburn[1] have slightly modified the method by the introduction of special precautions, and the results are considered by them to be more satisfactory than those obtained by Bailey and Baldsiefen.

The following table shows the percentages of insoluble bromides obtained from drying oils or their acids.

	From Glycerides.	From the Acids.
Perilla oil	53 per cent.	64 per cent. (Eibner)
Linseed oil, iodine value 181·0	23·1-23·5 ,,	42-50 per cent. (Steele and Bailey)
,, ,, 204·0	49·3 ,,	
,, ,, 190·4	37·72 ,,	
Tung oil	...	...
Menhaden oil	61·8 ,,	51·5 (Gemmell)
Soya bean oil	3·7	4·2-7·5 (Steele and Bailey)

Mixtures of linseed and fish oil can be detected by the characteristic fishy odour produced on heating. Small quantities, not below 5 per cent., can be detected by Eisenschiml's test,[2] which depends on the production of an insoluble octobromo-compound by the action of bromine at 100°. One hundred drops (about 5 c.c.) of oil are dissolved in 6 c.c. of a mixture containing equal parts of chloroform and glacial acetic acid. Bromine is added drop by drop until the brown colour remains. After ten or fifteen minutes the test tubes are placed in a beaker containing boiling water. Linseed and other vegetable oils

[1] *Ind. Eng. Chem.*, 1920, **12**, 52. [2] *Ibid.*, 1910, **2**, 43.

will become clear within a few seconds, while fish oils remain cloudy and give a precipitate of an insoluble bromide in a short time. Ten per cent. of fish oil can be recognised and, with experience, 5 per cent. Fish oils which have been heated to 260° for some time will not give this test owing to polymerisation of the oil.

Comparison of the Drying Time of an Oil against a Standard Linseed Oil. The method employed consists in the determination of the time of drying and the condition of the dried surface of a film of the oil after treatment with siccatives. In a recent War Office Specification (C. W. D./404, 1920) for raw linseed oil, nine volumes of the oil are mixed with one volume of a 25 per cent. solution of precipitated manganese resinate in turpentine, and the mixture exposed in the form of a thin film on glass, in a vertical position, at a temperature of 15°·5. The film must dry in a manner not inferior to that of a film of the approved tender sample, when tested at the same time and under identical conditions. Attention must be paid to the quality and appearance of the film, because some drying oils—*e.g.* perilla—give peculiar surfaces with irregular markings. It will be found in the comparison between Baltic linseed oil and Indian linseed oil that the film of a drying oil of the former variety is harder and dries in a shorter time under the same conditions. The iodine value of Baltic oil is always higher than that of Indian oil.

In the British Standard Specification[1] for Raw Linseed Oil (No. 243, 1926), the oil when tested in the following manner shall become surface dry in not more than four days at a temperature of 15°·6 to 21°·1.

Note.—By the term "surface dry" is understood such a condition that clean, dry, silver sand (graded so as to pass a 40 I.M.M. sieve but to be retained on an 80 I.M.M. sieve), sprinkled on to the surface of the oil film and allowed to remain there for about one minute, can be removed, without injury to the oil film, by means of a camel-hair brush.

"The oil shall be brushed on the ground surface of a ground glass panel about 4 in. (10·16 cm.) by 4 in. The panel shall be placed in a vertical position in a well-ventilated room at 60° to 70° F. (15°·6 to 21°·1 C.) and so arranged that its surface shall be illuminated by diffused daylight for at least six hours during each day of the drying period. In order to avoid interference through excessive humidity, care should be taken that throughout the drying process the temperature of the room is above the dew-point."

Mucilage. The determination of the mucilage is of importance as indicating whether the oil is fresh or has been tanked to allow the deposition of water and "foots." The amount present in a sample of oil can be determined in the following manner:—15 c.c. of the oil is placed in a test-tube ($\frac{5}{8} \times 6$ in.) and heated over an open flame

[1] Abstracted, by permission of the British Engineering Standards Association, from B. S. Specification No. 243, official copies of which can be obtained from the Secretary, 28 Victoria Street, S.W. 1, price 2s. 2d., post free.

to 300°, the temperature being determined by a thermometer suspended in the oil. The rise in temperature should not exceed 50 degrees per minute. A linseed oil containing mucilage "breaks" at 260°, and flakes of the mucilage appear. The oil is then cooled down to the ordinary tanked temperature and at once centrifuged in graduated tubes. A good linseed oil shows 2 to 3 per cent. mucilage by volume. If the oil is allowed to stand overnight after breaking, the "foots" cannot be removed by centrifuging. Other methods have been proposed by Walker and Wertz,[1] and C. D. Holley.[2]

Colour. The colour of linseed oil can be standardised by a Lovibond's tintometer (*see* Vol. I., p. 184). In the British Standard Specification for Raw Linseed Oil (No. 243, 1926)[3]:—

"The colour shall not be darker than that of a freshly-made solution of 0·1 g. iodine and 1 g. pure potassium iodide (free from iodate) in 100 c.c. water, when viewed transversely by transmitted light through a glass tube 1 cm. (0·39 in.) in diameter and about 10 cm. (3·94 in.) long.

"For refined linseed oil the colour shall not be darker than that of a freshly-made standard solution of 0·02 g. iodine and 0·2 g. pure potassium iodide (free from iodate) in 100 c.c. of water when viewed similarly."

Viscosity. The viscosity of a drying oil may be determined by any of the methods used for the determination of the viscosity of lubricating oils (*see* Lubricants, Vol. V.).

Detection of China Wood Oil in Linseed Oil. A modified elaidin test for the presence of tung oil in linseed oil devised by J. N. Goldsmith[4] is as follows:—1 c.c. of the oil is mixed with 5 or 6 c.c. of 10 per cent. acetic acid, 1 g. of solid sodium nitrite added and the mixture shaken vigorously. In the presence of as little as 10 per cent. of tung oil a buttery mass results, whereas linseed oil alone remains liquid. This test works in the presence of stand oil, perilla oil and also in the presence of rosin.

China Wood Oil (Tung Oil). Owing to the increasing demand for China wood oil the detection of adulterants in the oil is of importance. The commonest are soya, perilla, and lumbang (Aleurites) oils. The detection of the adulterants is based on (1) differences in optical dispersion, (2) polymerisation or gelation tests.

The high refractive index of China wood oil (1·5179 at 20°; linseed oil, 1·4835, 15°) and the refractive indices of soya and perilla approaching the value of linseed oil make it easy to detect adulteration.

The gelation test depends on the time taken for the oil under examination to set solid at a temperature of 293°. A sample of good tung oil should gelatinise in ten minutes when tested according to

[1] *Proc. Amer. Soc. Test. Mats.*, 17, Part I., p. 38. [2] *Drugs, Oils, and Paints*, 1916, p. 51.

[3] Abstracted, by permission of the British Engineering Standards Association, from B.S. Specification No. 243, official copies of which can be obtained from the Secretary, 28 Victoria Street, S.W. 1, price 2s. 2d., post free.

[4] *J. Oil and Col. Chem. Assn.*, 1926, 9, 342.

Browne's directions.[1] The presence of free fatty acids will extend the time required for gelation. It is possible to detect the presence of 5 to 10 per cent. of adulterating oil by means of the gelation test. The addition of lumbang oil will retard the solidification of the oil on heating, and also reduce the refractive index. Perilla oil raises the iodine value whereas soya depresses it, but both reduce the refractive index and retard the gelation of the oil.

In the heating test (Browne's Method) the test tubes for containing the oil should be 16 cm. by 15 mm., with a mark near the bottom to indicate 5 c.c., and closed by a cork so perforated that a glass rod 3 mm. in diameter can move freely. Fill a copper beaker (height 12 cm., internal diameter 6 cm.) with cotton-seed oil to a height of 7·5 cm., place a thermometer so as to be 1·5 cm. from the bottom of the bath. When the bath temperature is 293° and very slowly rising at this point, place the tube containing 5 c.c. of the oil to be tested so that its bottom is level with the lowest part of the bulb of the thermometer. Note the time, remove the source of heat for about forty-five seconds and then re-apply. Before two minutes have elapsed the temperature of the bath will have fallen to 282°, at which point it should be kept as steady as possible. When the tung oil has been in the bath about nine minutes, raise the glass rod at intervals of half a minute, and when the rod is firmly set note the time. As setting or jellying takes place within a few seconds of fluidity, a good end point is afforded. Remove the specimen at once, heat the bath again to 293°, and repeat the experiment with another portion of the sample. No stirrer is used in the bath. A screen around the bath enables the temperature to be more easily reached.

A raw tung oil should conform to the following requirements:—

	Maximum.	Minimum.
Specific gravity (15·5°)	0·943	0·939
Acid number	6	...
Saponification number	195	190
Unsaponifiable matter, per cent.	0·75	...
Refractive index at 25°	1·520	1·515
Iodine number (Hübl, 18 hours)	...	165
Heating test (Browne's method): minutes	12	...

Linseed Oil Substitutes.—The methods just described can also be employed in the examination of oils suspected of adulteration. When the price of linseed oil is high, adulterants appear. If the sample under examination has an abnormal drying time, specific gravity, iodine value and saponification value, adulterants may be suspected. The possible impurities are rosin oil, mineral oils, *e.g* benzine, kerosene or lubricating oil, fish oils, soya bean oil, corn oil, and hemp or rape oil. The cheapest and commonest adulterants are

[1] *Proc. Amer. Soc. Test. Mats.*, 1918, D, pp. 12-16, 577.

the mineral oils, which have lower specific gravity than linseed oil and reduce its saponification value. Rosin oil is frequently added to compensate for this reduction. The most objectionable linseed oil substitutes are those consisting of solutions of rosin and hydrocarbon oils with which are mixed tar oil and resin; such vehicles possess little permanence. Rosin would be indicated by the high acid value of the oil, and by the Liebermann-Storch test (*see* p. 565). Corn oil is sometimes used as a substitute in Canada, and as it is a semi-drying oil it will tend to delay the hardening of the film. The presence of soya oil will reduce the iodine value and the drying time. Other substitutes are obtained by dissolving metallic resinates in tar oil and petroleum. Raw soya oil as a substitute for linseed oil is preferably first blown, then given a heat treatment to thicken it, and a drier of manganese, lead and cobalt linoleates in the proportions of 0·03 per cent., 0·2 and 0·01 per cent. respectively. Such an oil is considered to be a fair substitute for linseed oil.

Table I.—Characteristics of Drying Oils.

	Sp. gr. (15° C.).	Refractive Index.	Acid Value.	Saponification Value.	Percentage Unsaponifiable Matter.	Iodine Value.	Bromine Value from Acids.	Viscosity
Linseed oil	0·932-0·9337	1·4831 1·4660 (60° C.)	1·3	190·2-195·2	0·65-1·1	170-20 (185 Wijs)	48·6-50·9	0·51 (poises) (25°)
China wood oil	0·9405-0·9420	1·5155-1·5207	3·3	192-196	...	168-178 (Wijs)	nil.	1·318 (poises) (25°)
Perilla oil	0·9343 0·928 (20° C.)	1·4841 (20° C.)	5·0	189-191	0·37	191-206	50·8-64·12	...
Menhaden oil	0·9272-0·9310	1·4803-1·4809	5-8	190-195	0·6-1·6	166-193	51·7	...
Para rubber oil	0·9249	1·475	0·6-5·0	189·1	...	135-139	6·7	...
Hemp oil	0·9270	1·48206	...	190-193	1·1	140-166	...	...
Poppy seed oil	0·9255	1·4586 (60° C.) 1·4751 (20° C.)	...	189-197	...	134-137	nil.	254-259 secs. 70° F. (Redwood)
Walnut oil	0·9259	1·4804	...	192·5	...	142-145	3·0	232 secs. (Redwood)
Soya oil	0·929	1·4680 (40° C.)	0·8-3·0	190-201	1·16	124-128	up to 7·8	...
Candlenut oil	0·927	1·4765	2·3	175-192	...	137-164	11·5-12·6	...
Lumbang oil	0·925-0·937	1·4928	4·4-7·1	190-194	...	160-164 (Hübl)	...	...
Chia oil	0·9333	1·4796 (25°)	1·8-3·8	192·2	1·0	190·6	...	...
Oiticica oil	0·94-0·9786	1·4945 (30° C.)	10·5-11·4	189-195	6·14	84-179	...	...
Niger oil	0·9338	1·4768 (15° C.)	...	189-192	...	127-134	...	263-298 at 70° F. (Redwood)

STAND OIL (LITHOGRAPHIC VARNISHES).

Stand oil and lithographic varnishes are obtained by heating drying oils, chiefly linseed oil, to 250° to 300° in the absence of air. Reference to the characteristics of polymerised linseed oil are shown in the following table:—

	Sp. gr. at 15°.	Saponification Value.	Iodine Value.	Oxidised Acids.	Percentage Hexa-bromides.
Raw linseed oil . .	0·9321	194·8	169·0	0·3	24·17
Tint varnish . . .	0·9584	197·5	113·0	1·5	...
Thin varnish . . .	0·9661	196·9	100·0	2·5	2·0
Middle varnish . . .	0·9721	197·5	91·0	4·2	...
Strong varnish . . .	0·9741	190·9	86·0	6·5	...
Burnt thin varnish* . .	0·9675	195·5	92·7	0·85	0·0

* Burnt thin varnish is made by heating the oil to its flash point and allowing it to burn quietly with constant stirring.

The percentage of thickened linseed or thickened wood oil in a mixing may be determined by the acetone solubility method, which depends on the fact that 50 per cent. of the oil thickened under works conditions is insoluble in acetone.[1]

VOLATILE THINNERS OF PAINTS, JAPANS AND VARNISHES.

For analytical purposes the term volatile thinners means solvents volatile in steam, and includes turpentine, white spirit, pine oil, and kerosene, together with aromatic hydrocarbons of benzene, toluene, xylene, etc., although kerosene requires special treatment for its complete expulsion from a paint or a japan (*cf.* p. 584).

For oil varnishes the most important thinners are turpentine, white spirit and kerosene. Some petroleums contain considerable amounts of aromatic hydrocarbons, and frequently hydrocarbons of the xylene type (solvent naphtha) are used because of their good solvent properties. The same thinners are mostly used in paints and in oil varnishes. In spirit varnishes methylated spirit, wood spirit, wood naphtha, butyl and amyl alcohols (fusel oil), benzyl alcohol, and esters, such as amyl acetate, are found. Ketones (acetone and higher ketones, *e.g.* acetone oil) are used as solvents for resins and for nitro- and acetyl-celluloses. Butyl acetate is an important solvent for nitro-cellulose.

Benzene mixed with methylated spirit finds its chief use in paint and varnish removers on account of its high solvent properties, and also in stains, to secure proper penetration. The solvent naphthas

[1] Morrell, *J. Soc. Chem. Ind.*, 1915, **36**, 105.

are used in enamel thinners and baking japans to secure the desired flow as well as for their great solvent power. Coal-tar naphtha is used as a solvent for pitches in the manufacture of bitumastic preparations. Light solvent naphtha (20 per cent. toluene and 80 per cent. xylenes) is used as a solvent for rubber. Heavy solvent naphtha (90 per cent. below 190°) is used as a solvent and thinner for quick drying paints such as antifouling compositions, and as a solvent for pitches. It is also used in conjunction with white spirit as a thinner for priming paints for woodwork. The examination of these substances will be dealt with in the order given above, beginning with turpentine.

Recently, hydrogenated derivatives of phenols and naphthalene have been introduced under the names of hexalin (cyclo-hexanol = hexahydrophenol), heptalin (methyl cyclohexanol), tetralin (tetrahydronaphthalene), dekalin (decahydronaphthalene), and tetralin extra (tetralin : decalin, 1 : 4).

The Determination of Volatile Thinners of Paints and Varnishes.

While the paint and varnish industry confined its requirements for volatile thinners to turpentine and white spirit, distillation in steam at 100° could be relied on to remove all the volatile thinner present, unless the product were a paste, semi-paste, or a short oil varnish, when an appreciable percentage of volatile thinner was retained in the product examined, due to the heavy consistency of the material.

A rapid method for the estimation of volatile thinners in a varnish is as follows:—3 to 4 g. of the varnish to be examined is weighed into a tared silica flask of about 200 c.c. capacity, containing a piece of broken glass or silica. The flask is about one-third filled with boiling water, and then heated to boiling over the free flame, a rotary motion being imparted to the contents of the flask. After about five minutes boiling the smell of the volatile distillate will have disappeared. The supernatant aqueous layer is poured off into a small separating funnel. If clear and free from floating oily globules, it may be neglected; if not, it is cooled, extracted with ether, returned to the flask, and the ether distilled off. The adhering varnish is freed from water by successive treatment with 10 to 15 c.c. of a mixture of three parts by volume of benzene to one part of methylated spirit, the flask being immersed up to the neck in a steam-bath, and the contents kept in continuous rotation until apparently free from volatile matter. This operation is repeated until the residue is clear when viewed by transmitted light. The loss in weight of the flask and residue gives the amount of volatile thinners.[1]

[1] De Waele and Smith, *Analyst*, 1920, 45, 328.

Where naphthas containing a considerable percentage of hydrocarbons boiling above 200° are present a special treatment is required. The sample must be heated in an oil-bath to 130° to 135°, and steam passed in. The addition of paraffin wax (melting-point 125° to 130° F.) may be advisable to maintain the mass in a freely fluid condition during the entire volatilisation of the thinner.[1] If the non-volatile vehicle contains a considerable percentage of linseed oil, it is advisable to redistil the volatile thinner in a current of steam, so as to free it from fatty acids before examination of the specific gravity, fractionation, and polymerisation.

Estimation of Turpentine.—The great demand for turpentine and the variety of its substitutes require careful control of the purity of the spirit. Each country has its own specification.

The British Standard Specification for American Turpentine is as follows[2]:—

"*Description.* The material shall be genuine refined turpentine as free as possible from colour and free from water and visible impurities.

"*Specific Gravity.* The specific gravity at 15°·6 C. (60° F.) shall be not less than 0·862 and not more than 0·872 when compared with water at the same temperature.

"*Distillation.* The material on distillation of 100 c.c. in the Standard Distillation Apparatus (*see* Fig. 52, Standard Distillation Apparatus) shall yield:—

Not more than 1 c.c. below 150° C. (302° F.) at 760 mm. pressure.
Not less than 95 c.c. below 170° C. (338° F.) at 760 mm. pressure.

"*Residue.* The amount of residue determined by evaporating 10 c.c. in a shallow, flat-bottomed dish about 4 in. (10·16 cm.) in diameter by 1 in. (2·54 cm.) deep on a bath of boiling water and subsequently heating for a period of two hours at 100° C. (212° F.) shall not exceed 2 per cent. by weight and shall be wholly organic.

"*Refractive Index.* The refractive index for the D line at a temperature of 20° C. (68° F.) shall be between 1·469 and 1·478.

"*Polymerisation.* The amount of residue left after polymerisation shall not exceed 10 per cent. by volume, and its refractive index shall be not less than 1·500 at 20° C. (68° F.). The polymerisation test shall be carried out as follows:—

"To 20 c.c. of concentrated sulphuric acid 96 per cent. (1·84 specific gravity) contained in a Leffman-Beam or Babcock Milk-Fat flask, the whole being immersed in iced water, 5 c.c. of turpentine shall be added drop by drop with frequent shaking, care being taken that the temperature does not rise above 60° C. (140° F.). When the mixture no longer warms up on shaking, the whole shall be thoroughly agitated and the vessel placed in a water bath and heated to

[1] Holley, *Paint Vehicles, Japans and Varnishes*, p. 116.

[2] Abstracted by permission of the British Engineering Standards Association, from B. S. Specification No. 244, official copies of which can be obtained from the Secretary, 28 Victoria Street, S.W. 1, price 2s. 2d., post free.

between 60° and 65° C. (140° F. to 149° F.) for ten minutes, the contents being thoroughly mixed by shaking vigorously five or six times during this period.

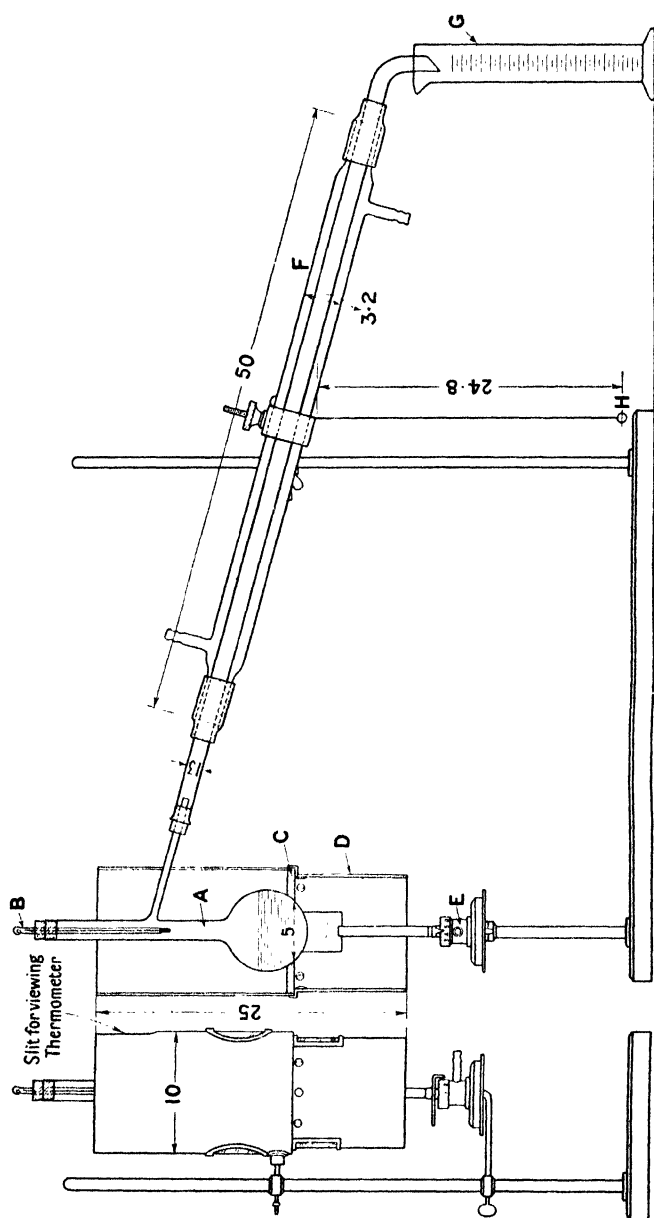



Fig. 52.

"The vessel shall be cooled to room temperature and sufficient of the concentrated sulphuric acid added to bring the level of the liquid into the neck

of the flask near the zero of the graduated scale, after which it shall be allowed to stand overnight (or it may be centrifuged) and the volume of the unpolymerised residue shall then be read off.

"*Flash Point.* The flash point (Abel's close test) shall be not less than 90° F. (32·2° C.)."

This polymerisation method (Armstrong's) has been modified to overcome the difficulty of separation of the products when the turpentine sample contains white spirit.[1]

V. E. Grotlisch[2] recommends for the polymerisation test 38 *N.* fuming sulphuric acid prepared from concentrated 95 per cent. and fuming sulphuric acids and containing more than 82·38 per cent. of total sulphur trioxide.

The American Specification[3] requires the following values for standard turpentine:—Sp. gr. (15°), 0·875 to 0·862; flash point (Abel) 86° to 88° F.; n_D (20°), 1·468 to 1·478; residue after polymerisation with 38 *N.* H_2SO_4, 2 per cent. (n_D 15°·5 = 1·5), (wood turpentine gives 2·5 per cent. (n_D 20° = 1·495)); initial boiling-point at 760 mm.: 160° (wood turpentine, 150°); percentage distillate below 170°, 90. The colour shall be "Standard" or better. The term "Standard" refers to the colour recognised as a standard by the "Naval Stores Trade." Turpentine is of "Standard" colour when a depth of 50 mm. in a perfectly polished bottom tube approximately matches a No. 1 yellow Lovibond glass.

Marcusson and Winterfeld[4] have put forward a method of estimating the amount of petroleum and aromatic hydrocarbons present in a sample of turpentine substitutes containing turpentine. Into a 100 c.c. flask provided with a long neck graduated in 1/10 c.c., 30 c.c. of fuming nitric acid (sp. gr. 1·52) is poured and cooled to −15° by ice and salt. By means of a dropping funnel 10 c.c. of the turpentine under examination is allowed to drop very slowly into the nitric acid. The greater the quantity of petroleum spirit present, the more quickly may the turpentine be introduced. About half an hour to one hour is required, according to the purity of the sample. The mixture is allowed to stand a quarter of an hour in the freezing mixture and the flask is filled up to the mark with concentrated nitric acid (not fuming), previously cooled to −10°, to remove any solid separating in the neck of the flask. The bulb of the flask must remain the whole time in the freezing mixture to avoid secondary reactions. The volume of the residue (petroleum) is shown in the graduated part of the flask to about 2 per cent. accuracy. The contents are now transferred to

[1] R. S. Morrell, *J. Soc. Chem. Ind.*, 1910, **29**, 241; Krieger, *Chem. Zeit.*, 1916, p. 427.
[2] *J. Soc. Chem. Ind.*, 1924, **43**, 878 B.
[3] *Proc. Amer. Soc. Test. Mats.*, 1918, D 13-15.
[4] Marcusson and Winterfeld, *Chem. Zeit.*, 1909, 987.

a separating funnel and the lower (nitric acid) liquid is withdrawn and poured into 150 c.c. water. Evolution of heat occurs and more or less oil separates out, according to the amount of the petroleum spirit. The aqueous liquid is heated for a quarter of an hour on a boiling water-bath and in a fume chamber to bring the resin from the turpentine completely into solution. After cooling, 100 c.c. ether is added, the water layer is withdrawn and the ether solution washed several times with water, then with caustic potash (10 per cent. potassium hydroxide and 10 per cent. alcohol), and finally with water. After drying the ether with calcium chloride, it is carefully distilled off and the residue weighed. The residue is a red brown oil possessing the aromatic smell of nitro-compounds.

The weight of the oil is divided by 1·15 to obtain the volume of the nitro-products of the aromatic and cyclic hydrocarbons, and this volume is added to the volume of the oil insoluble in the nitric acid fluid obtained above.

The disadvantages of this method are the violent reactions with nitric acid and the use of ice; moreover, the separation of the benzol from petroleum is incomplete, owing to the solubility of the nitro-compounds in petroleum hydrocarbons, while many petroleums contain appreciable quantities of aromatic hydrocarbons.

In the concentrated sulphuric acid method the polymerised product of turpentine is colophene, and the volatile unpolymerised material is cymene.

Another method for the estimation of turpentine devised by Tausch is based on the oxidation of turpentine by mercuric acetate. When pure turpentine is heated under a reflux condenser for three hours with mercuric acetate and methyl alcohol and then steam-distilled, no trace of turpentine is found in the distillate. The method may be used quantitatively, and the mercurous acetate formed may be collected, transformed into the chloride, and weighed. A blank experiment may be done with pure turpentine.

Salvaterra[1] suggests three suitable methods for the estimation of oil of turpentine:—

(1) Tausch's method. Twenty c.c. of the sample is introduced into a 2-litre flask containing 300 c.c. water and 20 c.c. 80 per cent. acetic acid. Fifty-one g. powdered mercuric oxide is slowly added, and then 10 c.c. methyl alcohol and the mixture heated with a reflux condenser on a water-bath for two or three hours and then steam-distilled, whereby the undecomposed hydrocarbons present as impurities are removed.

(2) By the action of hydrobromic and bromic acids at 20° to 25°, whereby the turpentine is rendered non-volatile in steam. If wood turpentine (Kienoel) be present, it is advisable to use a little more

[1] *Analyst*, 1921, **46**, 155; *J. Oil and Col. Chem. Assoc.*, 1920, **3**, 176.

hydrobromic acid. The method is unsuitable if tetralin (tetrahydronaphthalene) is present.

(3) By treatment of the spirit with iodine and mercuric chloride in alcohol, and keeping the mixture cool and in the dark for six hours. After addition of the concentrated solution of potassium iodide and excess of sodium thiosulphate, the solution is neutralised and finally distilled in a current of steam. The volatile impurities in the turpentine are found in the distillate. By the first method wood turpentine to the extent of 10 per cent. is volatile in steam, but not in the second and third methods. By applying both the mercuric acetate and either the bromine or iodine process it is possible to estimate the amount of pine oil in the adulterants.

The following results were obtained by Salvaterra in the examination of samples of turpentine containing solvent naphtha, benzine or tetralin, using Tausch's method:—

Volume taken.	Volume found.	Volume present.
20 c.c. . .	3·95 c.c.	4 c.c. (solvent naphtha)
20 c.c. . .	9·92 c.c.	10 c.c. (benzine)
20 c.c. . .	7·88 c.c.	8 c.c. (tetralin)

The table on the opposite page shows the important differences between the varieties of turpentine.

Manufacturers of wood turpentine now make a product that comes within the accepted physical and chemical limits of gum turpentine. The purchaser should, however, state whether gum or wood turpentine is desired. The presence of pine-tar oil (Kienoel) may be recognised by the fact that a fragment of caustic potash, brought into the liquid, will soon become coated with a yellowish brown layer, whereas in pure turpentine considerable time will elapse before the formation of such a layer. Oil which has become resinified should be distilled before the test is tried.[1] The presence of pine oil confers a pleasant aromatic odour suggestive of camphor or juniper. In amounts of not less than 10 per cent. it may be detected by the yellowish green coloration produced by sulphurous acid (Herzfeld's reaction). A test for rosin spirit in turpentine has been described by P. H. Conradson.[2] An aqueous solution of sulphurous acid, when shaken with rosin spirit, colours the latter yellow. Turpentine, benzene, gasolene and 160° oil give no such colouration. Rosin essence may be recognised, apart from the low temperature at which the turpentine begins to boil, by Grimaldi's reaction,[3] which depends upon the collection

[1] Herzfeld, *Z. öffentl. Chem.*, 1903, 9, 456; 1904, 10, 382.
[2] *J. Soc. Chem. Ind.*, 1897, 16, 519.
[3] *Chem. Zeit.*, 1907, 92, 1145.

Table II.—Varieties of Turpentine

	American Oleo-Resin Turpentine.	Steam-distilled Wood Turpentine.	Destructive-distilled Wood Turpentine.	French Turpentine.	Greek Turpentine.	Spanish Turpentine.	Russian Turpentine.	Indian Turpentine (Quality 1).
Sp. gr. (15°·5 C.)	0·8617-0·889	0·859-0·915	0·862-0·867	0·857-0·872	0·8602	0·869	0·862-0·875	0·865
Colour	Water white	Water white	Colourless or slight yellow	Colourless	Pale straw	Dark amber	Colourless or yellow	Colourless
Flash point	89° F.	91° F.	...	86-90° F.	83° F.	91° F.	95°-100° F.	103° F.
n_D 20°	1·4684-1·4818	1·4673-1·4755	1·467-1·469	1·468-1·478	...	...	1·476	1·481
a_D 20°	−34°·8 → +29°·6	+16°·5 to +36°·14	+34°·4 → +77°·6	−20° → −40°	+36° → +46·5	as French	...	+2·48
Polymerisation residue	2 per cent.	3-4 per cent.	2·3 per cent.	...	...	...	...	...
Initial boiling-point	154°-159°	153°-177°	143°-160°	155°	124°	130°	160°	...
Below 170°	Above 90 per cent.	90 per cent.	...	at 160° 77·5 per cent.	78 per cent.	88 per cent.	87 per cent.	80-90 per cent. at 170°
Below 180°	88-99	98 per cent.	at 180° 85 per cent.	at 170° 92·5 per cent.	...	94·5 per cent.	96 per cent.	...
Iodine value (Wijs, ½ hr.)	350-400	282-352	300-398	...	...	...	...	...

of fractions of oil, in amounts of 3 c.c. each up to 170°, and the production of a green coloration with tin and hydrochloric acid.[1]

From the data given it will be evident that the preference for American turpentine is largely due to its uniform quality and characteristic smell. The differences in properties between it and French turpentine are not important, and prejudice is powerful in the selection of a variety. Thus Indian, Greek, and Swedish suffer in comparison, and in Russian turpentine the large amount of greasy residue left on evaporation, together with its variable colour and essentially marked characteristic odour, render its use in high class paints and varnishes primarily local or in the country of origin.

Pine Oil.—The term pine oil as now understood is the heavy oil obtained from the fractionation of crude steam-distilled wood turpentine. It is also obtained as a by-product in the manufacture of wood pulp by the sulphite process. Good quality pine oil has a pleasant aromatic odour, but inferior qualities cannot be used for indoor work on account of the obnoxious odour of the empyreumatic compounds which they contain. It is a powerful solvent for resins, and has strong penetrating properties like solvent naphtha.[2] It contains a high percentage of terpineol, $C_{10}H_{18}O$, from which terpine hydrate, $C_{10}H_{20}O_2 + H_2O$ can easily be obtained. The following are the chief characteristics of light straw-coloured pine oil:—Sp. gr. at 15°, 0·932-0·935; refractive index at 20°, 1·4798-1·4830; distillation range, 90 per cent. between 190° and 218°; acidity, below 0·1 per cent.; flash point 76°.

Turpentine Substitutes.—The requirements for a good turpentine substitute are solvent power equal to that of turpentine and equally rapid air-drying, only a small amount of greasy non-volatile residue being left; the smell must be pleasant and resemble that of turpentine; the flash point must be above 73° F. to conform with transport requirements. As far as possible, the rate of evaporation of the substitute must correspond with that of turpentine, and, if the substitute be a blend, the less volatile components must have a solvent power for resins and oils equal to that of turpentine. The majority of turpentine substitutes are essentially petroleum, blended in varying amount with turpentine. The petroleums are generally not such good solvents for resin oil mixings or metallic driers, nor have they the same viscosity and flow as turpentine. Certain natural petroleums have a solvent power of a high order, but their thinning powers are greater than turpentine, which is a disadvantage. The petroleums are so varied in composition that for comparison volatility tests are usually relied on. The presence of aromatic hydrocarbons generally tends to improve

[1] Wolff, *Chem. Zeit.*, 1912, 36, 64; *J. Soc. Chem. Ind.*, 1912, 31, 692; Piest, *Chem. Zeit.*, 1912, 36, 198; *J. Soc. Chem. Ind.*, 31, 1912, 239.

[2] M. Toch, *Ind. Eng. Chem.*, 1914, 6, 720.

the solvent power of the turpentine substitute. Details of the estimation of petroleums in the presence of turpentine have already been given, but it is advisable to quote the specifications of white spirit for British American and French requirements. The following British Standard Specification for White Spirit, Type 1 for Paints (1926), may be taken as the most recent for white spirit as a turpentine substitute in thinning paints and varnishes.[1]

"*Description.* The material shall be wholly a petroleum product. It shall be water-white, clear, free from water and other visible impurities; also free from objectionable odour.

"*Flash Point.* The flash point (Abel's close test) shall not be less than 78° F.

"*Distillation.* The material on distillation of 100 c.c. in the Standard Distillation Apparatus (*see* Turpentine) shall yield not more than 10 c.c. below 150°, not less than 80 c.c. below 190°, not less than 90 c.c. below 200°.

"*Freedom from Grease.* No grease spot or mark shall be visible on the paper when 3 or 4 c.c. are allowed to fall on a sheet of ashless white filter paper, 20 cm. by 20 cm., and the paper is freely exposed to the air for one hour at a temperature not exceeding 60° F. (15°·5 C.).

"*Residue.* The amount of residue determined by evaporating 50 c.c. in a flat-bottomed dish (about 4 in. in diameter) on a bath of boiling water for a period of four hours shall not exceed 0·2 per cent. by weight and shall be wholly organic.

"*Neutrality Test.* When 50 c.c. of the material is shaken with 10 c.c. of distilled water the water layer shall remain neutral to methyl orange.

"*Freedom from Objectionable Sulphur Compounds.* The material shall be free from objectionable sulphur compounds as indicated by there being no change in the colour of freshly cleaned copper strips kept in the distillation flask during distillation, carried out as specified in the distillation clause."

Coffignier recommends the following fractionation value for white spirit:—

	Per cent.		Per cent.
70°-100° C.	0·1	160°-170° C.	35-36
100°-130°	1·52	170°-180°	18·5-26
130°-140°	10-17·5	180°-190°	10-17
140°-150°	31-48	190°-200°	0-7
150°-160°	56·5-69		

A high grade white spirit gives generally between 5 and 10 per cent. non-volatile material above 200°. War Office Specification (C.W.D. 406) for white spirit for use in paint and for cleaning shells requires 80 per cent. distillate at or below 200°.

[1] Abstracted by permission of the British Engineering Standards Association, from B. S. Specification No. 245, official copies of which can be obtained from the Secretary, 28 Victoria Street, S.W. 1, price 2s. 2d., post free.

The estimation of the amount of petroleum and aromatic hydrocarbons present in a sample of turpentine substitute containing turpentine has been described on p. 586, and the precautions to be taken to avoid loss of the petroleum and aromatic hydrocarbons pointed out. The percentage of aromatic hydrocarbons present in the petroleum spirit may be determined by Henriques' fuming sulphuric acid method,[1] which consists in mixing 5 c.c. of the sample with 10 c.c. concentrated sulphuric acid containing 10 per cent. SO_3 in a stoppered cylinder graduated to 0·2 c.c. The undissolved portion after agitation of the mixture at the ordinary temperature will be a measure of the non-aromatic hydrocarbons present. It must be remembered that nearly all petroleum hydrocarbons in petroleum substitutes are more or less soluble in fuming sulphuric acid; moreover the non-aromatic hydrocarbons are appreciably soluble in aryl sulphonic acids though not in sulphuric acid. White spirit gives 8 per cent. contraction; kerosene, 16 per cent.; Rumanian petroleum spirit, 48 per cent.; and xylene petroleum spirit as much as 54 per cent. absorption by fuming sulphuric acid.

F. B. Thole[2] estimates benzene and toluene in petroleum by shaking one volume of a toluene-petrol or benzene-petrol under examination with three volumes of 98 per cent. sulphuric acid in a 50 c.c. cylinder. External cooling is necessary only with mixtures rich in aromatic compounds. For mixtures richer than 50 per cent. benzene-petrol it is advisable to separate the supernatant unabsorbed spirit and treat it with a fresh quantity of acid in order to avoid errors due to incomplete separation and absorption of the non-aromatic hydrocarbons by aryl sulphonic acids formed by the sulphuric acid. Thole recommends the determination of the specific gravity of the initial fraction and of the residual spirit after acid treatment. Knowing the specific gravity of the aromatic component the percentage present may be calculated from the formula:—

$$\text{Percentage aromatic} = \frac{\text{Initial sp. gr.} - \text{final sp. gr.}}{\text{Sp. gr. of aromatic} - \text{final sp. gr.}} \times 100.$$

The aromatic hydrocarbons are assumed to be benzene and toluene. The presence of olefines and diolefines introduces complexities which have not been dealt with, since the method is only designed for the analysis of straight-run distillates from a crude oil. In petroleums containing naphthenes, aromatic hydrocarbons, and sulphur compounds the estimation of the aromatic hydrocarbons is difficult. In the first place it is necessary to remove the sulphur and unsaturated compounds without affecting the benzene and toluene before the estimation of the aromatic hydrocarbons can be begun. The unsaturated compounds can be removed quantitatively by boiling with

[1] *Chem. Zeit.*, 1895, p. 958. [2] *J. Soc. Chem. Ind.*, 1919, **38**, 39 T.

an 80 per cent. sulphuric acid solution for about half an hour in a flask under a reflux condenser, the neck of the flask being composed of a graduated burette in which the losses sustained in the operation can be read directly. The sulphur compounds are decomposed by prolonged boiling under the reflux condenser until no more hydrogen sulphide is evolved. The residual sulphur compounds after this treatment are practically unacted on by strong sulphuric acid. Having thus cleaned the original sample, the distillate is treated with acid and the aromatic compounds estimated by substantially the same method as outlined above by Thole[1] (p. 592).

The "formolite" reaction may be found useful in the examination of volatile thinners. The reaction is carried out by mixing 1 vol. of the liquid to be tested with 2 vols. methylal and adding drop by drop 2 vols. concentrated sulphuric acid. The solution becomes warm and each drop of acid produces a momentary red colour, and a sludge forms. On pouring the mixture into about 300 c.c. of cold distilled water and making just alkaline with ammonia, the formolite separates as a light brown solid, which may be filtered off, dried at 100° and weighed. A preliminary drying over sulphuric acid is desirable.[2]

L. G. Radcliffe[3] was able to detect 1 per cent. of benzene in a light petroleum spirit. White spirit and also turpentine give heavy "formolite" precipitates.

It is evident that the estimation of a turpentine substitute containing turpentine and a mixture of aromatic and petroleum hydrocarbons is not very accurate. The method of Armstrong, Marcusson and Winterfeld, and two out of the three methods recommended by Salvaterra are not accurate in the presence of aromatic and unsaturated petroleum hydrocarbons. The method of Tausch is perhaps the most free from error. Until reliable methods of estimation of aromatic compounds in petroleum mixtures have been accepted, it is impossible for the paint and varnish analyst to state accurately the percentages of the petroleum and aromatic components present in admixture with turpentine.

Hexalin, Heptalin, Tetralin, and Dekalin.

The introduction of new thinners such as tetralin, dekalin, hexalin (cyclohexanol), and heptalin (methylcyclohexanol), renders the examination of a petroleum substitute more complicated.

The following characteristics of the four solvents just mentioned suggest that these properties serve for an indication of their presence although no methods of quantitative estimation in admixture with

[1] Hackford, *J. Soc. Chem. Ind.*, 1919, 38, 42T.
[2] Fox and Bowles, *loc. cit.*, p. 155.
[3] *Perf. Essent. Oil Rec.*, 1920, 11, 48.

turpentine and petroleum are as yet available. Hexalin and heptalin may be estimated by Verley and Bolsing's method.[1]

	Boiling-point.	Sp. gr.	Flash Point.	Refractive Index at 20° C
Tetralin . . .	205-207°	0·975-0·977	75° C.	1·540
Dekalin . . .	185-195°	0·890	60°	1·467
Hexalin . . .	160°	0·945	68°	1·468
Methylhexalin .	160-180°	0·927	68°	1·463

For other properties reference may be made to N. Heaton[2] and H. Wolff.[3]

Solvent naphthas (*cf.* p. 588) when present in a turpentine substitute behave essentially as aromatic hydrocarbons. The following table shows the characteristics of benzol, xylol, and solvent naphtha.

Solvent naphthas are fractions obtained in the distillation of coal, and consist of liquids containing solid hydrocarbons. The methods of Colman, Northall-Laurie, and Jones,[4] can be used for the estimation of benzene, toluene, and xylene in solvent naphtha.

	Boiling-point Limits.	Sp. gr. (15°).	Flash Point (°C.).
90 per cent. benzol . .	90 per cent. up to 100°	0·880 883	below – 4°
	100 ,, ,, 120°	...	...
50 per cent. benzol . .	50 ,, ,, 100°	0·875 877	...
	90 ,, ,, 120°	...	...
0 per cent. benzol (toluol)	0 ,, ,, 100°	0·870 872	...
	90 ,, ,, 120°	...	...
Heavy benzol . . .	0 ,, ,, 160°	0·920 945	47°
	90 ,, ,, 195°	...	...
Xylol (crude) . . .	90 ,, ,, 120-150°	0·867 869	...
Xylol (purified) . .	90 ,, ,, 138-142°	0·86	21°
Solvent naphtha I. . .	0 ,, ,, 130°	0·878 880	21°
	90 ,, ,, 160°	...	...
Solvent naphtha II. .	0 ,, ,, 145°	0·880 910	48°
	90 ,, ,, 175°	...	...

For the characteristics of other varnish solvents, *e.g.*, wood spirit, alcohol, fusel oil, amyl acetate, ketones, chlorinated hydrocarbons (tetrachlorethane), etc., reference may be made to the special articles dealing with these substances.

[1] *J. Soc. Chem. Ind.*, 1901, **20**, 1250.
[2] Volatile Solvents and Paint Thinners, 1925.
[3] *Die Lösungsmittel der Fette, Oele Wachse u. Harze*, 1922.
[4] *J. Soc. Chem. Ind.*, 1917, **36**, 489.

Balsams and Resins.

Balsams and resins are secretion or excretion products of plants formed during the course of metabolism, either under normal conditions or caused by disease; they are mixtures of varying composition. Balsams contain resin dissolved or emulsified in ethereal oils; they are more or less fluid and exhibit strong characteristic odours. The resins may be considered as oxidation products of essential oils, and their consistency varies according to the relative proportion of the different constituents. Gum resins may be distinguished from gums by the following simple tests:—(1) When a resin is held in a flame it takes fire and burns with a smoky flame giving off an aromatic odour; a gum similarly treated chars and smells of burnt sugar. (2) A resin placed in water is unaltered, whereas a gum dissolves or forms a jelly. (3) When a resin is allowed to stand in methylated spirit or in turpentine it disintegrates or dissolves completely or partially. A gum is generally unacted on by these solvents. The gums, *e.g.* gum arabic, gum tragacanth, are essentially carbohydrates and yield sugars on hydrolysis. The balsams are solutions or emulsions of resins in oil esters, *e.g.*, the esters of cinnamic or benzoic acids; they may contain also free cinnamic and benzoic acids. The oleoresins consist of resins associated with essential oils. It is difficult to draw a hard-and-fast line between the two classes by differences in the nature of the resin solvents. The balsams are essentially more fluid than the oleoresins, although certain varieties of oleoresins when freshly exuded have considerable fluidity, so that the oleoresin may be said to be exuded in the balsamic form, hardening on exposure to the viscous solid oleoresin. The transformation of a balsam into an oleoresin may be a combination of oxidation and a polymerisation resembling the transformation of the latex into solid rubber. The differences are perhaps rather of degree, although balsams often contain a high percentage of oil esters. Canada balsam is classed amongst the oleoresins rather than the balsams. Copaiba balsam contains 40 to 60 per cent. essential oil, and the remainder is a resin. Gurjun balsam consists of a resin and an essential oil (40 to 82 per cent.), which is a sesquiterpene ($C_{15}H_{24}$). Storax contains styrolene, cinnamic acid, cinnamyl cinnamate, styricine, myrocarpene and a resene.

The methods employed to obtain the balsams and resins are usually so crude that the substances which come on the market as resins, balsams, and gum resins are completely changed products differing widely from their original form as they occur in nature. On account of the great distances from which they come, the many hands through which they have to pass, and their completely changed and varying composition, the examination of samples obtained direct from the tree and of authenticated purity is extremely useful and of

fundamental importance. The analytical data obtained from such genuine samples, *e.g.* Peru balsam, have led to definite conclusions, but have also shown that the commercial article very seldom corresponds to the genuine resin. A demand for the genuine resin would lead to the rejection of nearly all commercial samples.

Hence in the examination of commercial samples certain variations must be allowed, and concordant results, such as are obtained in the fats and oils, must not be expected. Unfortunately the analyses of resins not only vary within wide limits, but are occasionally contradictory. For this reason it is difficult to lay down reliable methods of examination or even to fix certain limits within which characteristic values may vary.[1]

The perusal of technical literature dealing with resins and lac reveals the fact that except for shellac and rosin only one definite attempt[2] has been made to draw up standards as a basis for purchase, but the advent of synthetic resins or lac products will in time compel more careful examination of natural resins or their market varieties. The important properties of the resins are colour, hardness, lustre, and specific gravity, as well as solubility and melting-point. Among the chemical characteristics are acidity, saponification value and iodine value. Of these, W. B. Parker considers that the following are suitable for use in specifications—colour, size, cleanliness, habit (when of positive value), solubility in various solvents, moisture content, ash, iodine value, acid and saponification values. The hardness of resins is of importance, but as yet the results are so uncertain as to render them of little value for standardisation. Preliminary specifications for the different varieties of shellac, dammar, manila copal (spirit soluble), and kauri have been drawn up by Parker, and the following table gives the details of the characteristics of the above resins:—

	Solubility in Methylated Spirit. Sp. gr. of Solution 0·925.	Ash.	Iodine Value (Hübl)	Acid Value.	Saponification Value.	Wax (Extracted by Petrol-ether).
		Per cent.	24 hrs.			Per cent.
Pure button lac	160 pts. in 246 pts. Methylated spirit	not above 0·6	8·0	66	225	3-6
Black button lac	,, ,,	,, 2·0	14·0	66	225	3-10
Lemon shellac	,, ,,	,, 0·7	7·5	60	200	3-6
T. N. shellac	,, ,,	,, 1·5	14·0	66	225	3-9
Pure orange	,, ,,	,, 1·0	9·0	60	200	3-8
Kauri (genuine N.Z.)	...	,, 0·5-5·5	90-125	34-110	70-115	...
Manila (spirit soluble)	90 per cent.	,, 0·25	98-152	120-160	140-230	...
Dammar (East Indian)	71 per cent. (Coffignier)	,, 0·25	20-60	20-70	60-140	...

[1] K. Dieterich, *Analysis of Resins, Balsams, and Gum Resins*, 2nd Eng. Ed., 1920; T. H. Barry, A. A. Drummond and R. S. Morrell, *Natural and Synthetic Resins*, 1926.

[2] W. B. Parker, *J. Oil and Col. Chem. Assoc.*, 1922, 5, 208.

It is evident from the figures given that there is great variation in the iodine, acid and saponification values, and the figures given by Parker are not sufficiently definite for standardisation. He criticises adversely the results obtained by the Amer. Soc. Test. Matls. and British Eng. Standards Assoc. in their specifications of shellac. It must be confessed that the chemical characteristics of resins require further investigation. Coffignier, who has investigated the properties of resins for a number of years, states that the superficial examination by experts is rarely at fault, and that most of the resins used in varnish-making are obtained on their recommendations. Much is to be said for Coffignier's views, but batches have been known in which a closer attention to analytical values would have avoided undesirable properties in special varnish mixings. It will not help the elucidation of varnish problems if the resins are bought on superficial examination, so that in the mixings the special properties of the resin depending on chemical composition are ignored. In a colloid mixing, variation in chemical composition, however slight, may have great effect on the resulting film, and the acidity of a resin may have a decided influence on the oil with which it is incorporated.

Table III.—Chemical and Physical Characteristics of Resins.

(Barry, Drummond and Morrell.)

	Sp. gr.	Per cent. Insoluble in Alcohol.	Acid Value.	Köttsdorfer Value.	Iodine Value.
Copals:—					
Zanzibar	1·058	83·8	60-123	75-92	79
" fused	...	...	61	87	127
Madagascar	1·056	92·6	48-78	66-83	...
Demerara	...	67·2	97	98-110	50-55
Benguela	1·058	16·5	123-134	73-157	61-85
Angola (red)	1·066	37·6	128	130-147	63-137
" (white)	1·055 (17° C.)	15·1	127	115-160	130
Accra	1·033 (27° C.)	47·0	85-98	132	122-143
Cameroon	1·052 (27° C.)	67·0	160	157	65-66
Kissel	1·066 (27° C.)	57·0	70	118	...
Sierra Leone	1·0645	62·0	110	115-130	63-138
Kauri (brown)	1·053	46·0	70-93	79	177
" (bush)	1·03	12·0	51-83	83	...
Congo (hard)	1·061	25·3	132	124-132	58-59
Brazil	1·053	30·0	123-149	132-153	123-134
Manila (hard)	1·065 (17° C.)	3-56	72-141	87-215	90
" (soft)	...	2·0	145	187	106
Amber	1·080	86·0	97-140	115-154	62
Sandarach	1·073	Soluble	139-154	154-157	134
Mastic (tears)	1·057	16·8	50-70	70-79	64
Dammar (Batavia)	1·031	28·50	19-35	20-47	64
" (Singapore)	1·057 (18° C.)	19·10	30	39	123
Pontianai	1·037 (16° C.)	Soluble	134	186	119-142
Resin	1·07	Soluble	165-185	168-176	116-257
Shellac (stick lac)	1·009 (16° C.)	14·4	34·7	173·9	16

Table IV.—Chemical and Physical Characteristics of Resins.

Resin.	Raw.				Sweated at 300° C.			
	Acid Value.	Kötts-dorfer Value.	Per cent Unsap. Matter.	Iodine Value.	Acid Value.	Kötts-dorfer Value.	Per cent. Unsap. Matter.	Iodine Value.
Sierra Leone	72	119	18·8	106	13	115	17	125·5
Manila	127	175	16	138	68	136	23	133·3
Brazil	109	171	7·6	128	46·25	114	38·7	137
Kauri	37·4	54	20	91	17	61	10	67·7
Animi 1	18·7	73	6·3	103	...	58·7	...	106
Animi 2	30	32·7	76	127·5	...	...	...	...
Amber	16·7	121·7	19	59	...	...	...	...
American resin	158	182	0·75	122	146	153	16	134
Shellac (dark)	61	203	3·6	36·5	...	...	...	...
Dammar	35	32·7	76	127	11	60	86·6	127
Sandarach (Mogador)	134	143	13·2	112	65	136	14·3	126
Mastic	52·7	83	51	175	23·2	50·2	49	165

Acid Value. Direct titration is preferable, but it is often desirable to use both direct and back titration, because useful information frequently results from the double test. In the determination of the acidity of resins a neutralised mixture of equal volumes of purified 90 per cent. benzene and denatured alcohol may be used as solvent.[1] Uncertainty of end-point in the titration is overcome by allowing the solution to stand for one or two minutes, and observing the upper layer of oil and solvent, which at the neutralisation point should be clear and faintly pink. Titration of the cold solution is carried out after the resin has been heated to boiling for a few minutes with the solvent.

Saponification Value. In the determination of the saponification value H. Salvaterra[2] recommends precipitation by barium chloride of the soaps formed in the saponification, which decolorises the solution and enables the end-point of the titration to be decided more easily.

Iodine Value. The determination of the iodine value of resins may be instanced by the American standard method for the determination of resin in shellac.[3]

Ground shellac (0·2 g.) is introduced into a 250 c.c. dry glass stoppered bottle, 30 c.c. glacial acetic acid added (melting point 14°·7 to 15°), and the mixture gently warmed until solution is complete (except for the wax). A pure shellac is soluble with difficulty, and more rapid solution is the greater the proportion of resin present.

[1] H. A. Gardner and R. E. Coleman, Circ., 87, Paint Manuf. Assoc., U.S.A., 1920; *J. Soc. Chem. Ind.*, 1920, 39, 306A.

[2] *Chem. Zeit.*, 1919, 43, 765; *J. Soc. Chem. Ind.*, 1920, 39, 72A.

[3] *A.S.T.M. Standards*, 1918, p. 610.

Ten c.c. pure chloroform is added and the solution cooled to 21°, 25 c.c. Wijs's iodine monochloride solution added, and the mixture kept in the dark for one hour at 21°. Twenty c.c. of a 10 per cent. solution of potassium iodide is then added, and the excess of iodine titrated with standard sodium thiosulphate. A blank experiment must be carried out with all the reagents in the same manner, and the percentage of iodine absorbed calculated. When rosin or other resins are suspected in quantity, the amount of the sample used in the test should be kept near to 0·15 g. According to the American specification no pure shellacs show a higher iodine value than 18. According to the British Standard Specification for Aircraft Material the shellac in a shell varnish must have an iodine value not exceeding 32, when determined by the method described above.

From the iodine value of a sample of shellac, if the iodine value of rosin be taken as 228, and that of pure shellac as 18, the percentage of rosin in the sample is given by the formula :—

Iodine value of shellac = 18; Iodine value of rosin = 228; Iodine value of mixture = x.

$$\text{Percentage of rosin} = \frac{x - 18}{228 - 18}.$$

The importance of the iodine value of resinous material is indicated in the estimation of the purity of shellac. Parker, speaking from considerable experience, has found it a good guide to the nature and purity of practically every resinous substance. Owing to the colloidal character ot most resinous materials the rapid methods of Wijs and Hanus are unsatisfactory. The best method is the Hübl, the best "duration" is twenty-four hours, and the iodine should be in considerable excess (not less than 150 per cent. excess). With the Wijs reagent the results may be twice as high as those obtained with the Hübl solution, and vary greatly with the temperature, time of contact, and proportion of the reacting substances (see p. 571).

Solubility. The method used for the solubility of shellac in benzene may be taken as typical of the determination of the solubility of resins in non-aqueous solvents. About 1 g. of the resin is powdered and added to 100 c.c. of crystallisable benzene. The mixture is heated to about 70° for one hour with frequent shaking, after which it is cooled in water to a temperature of 7° for two hours. The clear benzene is decanted and the residue washed twice with benzene, dried and weighed.

Moisture. For the determination of moisture in a resin the method used for bleached shellac may be taken as typical. Both orange and bleached shellac give off volatile matter at temperatures approaching 100°.

Bleached shellac alters chemically at these temperatures, losing its solubility in alcohol. The usual methods of determining moisture by heating in an air-bath at 100° to 110°, are not applicable in the analysis of shellac. It is advisable to dry the powdered shellac in a vacuum to constant weight, and to weigh rapidly, for the lac is very hygroscopic. Another method is to dry shellac at 38° to 43° for three hours in a well-ventilated air-bath, taking care not to allow the temperature to rise above 43°, otherwise sintering occurs, which retards the drying.[1]

Owing to the high price of shellac, adulteration with spirit-soluble resins, *e.g.* manila and rosin, is common. The Liebermann-Storch reaction (p. 565) is applicable to decide the presence of above 5 per cent. of rosin. The characteristic aromatic odour of manila resin is noticeable if the resin is gently heated.

Reference may be made to the examination of a few balsams and resins for the detection of common impurities.

Copaiba Balsam.—The balsam is a thin (Para-balsam) or thick (Maracaibo-balsam) oily fluid with a greenish fluorescence. The addition of fatty oils as adulterants may be recognised by incomplete solution in 80 per cent. chloralhydrate solution. Other impurities are Gurjun balsam and turpentine oleo-resin. On distillation in a current of steam a genuine Copaiba balsam gives a volatile oil showing an optical rotation of $-7°$ to $-35°$ for 100 mm. Maturin copaiba balsam is now used as a substitute for the Maracaibo variety.

Gurjun Balsam.—The balsam is a cloudy fluid with a green fluorescence. The specific gravity and consistency vary with the proportion of ethereal oil (45 to 70 per cent.). Gurjun balsam may be recognised by the following colour tests:—(*a*) one part balsam, twenty parts carbon disulphide and 0·2 (H_2SO_4, HNO_3; 1 : 1) give a red-violet colour; (*b*) one part balsam dissolved in three or four drops of glacial acetic acid and one drop of 10 per cent. sodium nitrite when covered with concentrated sulphuric acid gives a dark violet colour.[2]

Acaroid Resin is generally too cheap to have any adulterants, and in **dammar resin** the common impurity is rosin.

Sandarac.—A test for sandarac is given by J. F. Sacher:[3]—The resin free from solvent is treated with ether, the filtered ether solution evaporated down and the residue treated with a mixture of ten parts of ether and thirteen parts concentrated sulphuric acid to give a reddish brown clear liquid. Without cooling, half its volume of water is added to the liquid and the presence of sandarach is indicated by a characteristic odour.

[1] *A.S.T.M. Standards*, 1918, p. 615.
[2] Utz, *Farben-Zeit.*, 1913, 18, 2531.
[3] J. F. Sacher, *ibid.*, 1916, 21, 188.

Elemi.—The resin has a characteristic smell and it may be also identified by preparing amyrin ($C_{30}H_{45}OH$) from it. The resin or mixture of resins is finely powdered, shaken with ether, and the ether solution repeatedly extracted with 20 per cent. caustic potash. After evaporation of the ether and digestion of the residue for several days with cold alcohol, the insoluble residue is recrystallised with ether and alcohol to give crystalline needles of amyrin (melting point 170°). The method is not quantitative.

Japan Lac.—A method of examination of a sample of Japan lac has been devised by Majima. One g. of the sample is warmed on the water-bath to transparency, and then heated thirty minutes in a steam-heated drying oven; this gives the percentage of water by the loss in weight. The dried residue is extracted with absolute alcohol, and the filtrate neutralised with *N*/4 $Ba(OH)_2$. Urushiol separates out as an insoluble barium compound. The difference between the weight of dry substance and the weight of the urushiol will give the weight of the oil in the sample.

Mastic.—The presence of sandarac will be shown by incomplete solution of the resin in benzene. Rosin can be detected in the usual manner.

Estimation of Resins in Mixtures.

The estimation of resins in a mixture by chemical methods is not conclusive. The iodine value, acidity, and saponification value give indications, but the composition will be speculative and it is only in the special case of shellac with rosin that the results can be relied on. The identification of the resin in all oil varnishes is difficult, as will be seen in the discussion of the methods of varnish analysis.

Stewart[1] has put forward a method of estimation of dammar and kauri mixtures, which depends on the extraction of the resin by absolute alcohol in a Soxhlet apparatus. The solubility of kauri in absolute alcohol is 91·56 per cent., whereas the solubility of dammar is 58·28 per cent. The insoluble component of dammar, 36·4 per cent., is however completely soluble in chloroform. The method of analysis consists in extraction by absolute alcohol followed by extraction of the insoluble residue with chloroform.

H. Ingle[2] has devised a method for determining quantitatively kauri, manila, and dammar in admixture by means of the acid value and solubility in carbon disulphide. Kauri, manila, and dammar gums have acidities 50 to 70, 107 to 156, and 30 to 32 respectively, and on boiling each of the gums with a 5 per cent. sodium carbonate solution, acidulating and weighing the precipitated acids, the yields were 6, 93, and 2·5 per cent. respectively. Kauri and manila are completely

[1] *J. Soc. Chem. Ind.*, 1909, **28**, 349.

[2] *J. Soc. Chem. Ind.*, 1912, **31**, 272.

soluble in benzene-alcohol (1 : 3), whilst dammar leaves 36 to 44 per cent. insoluble, but dammar is soluble in carbon disulphide. A mixture of 50 per cent. kauri, 25 per cent. dammar, and 25 per cent. manila when boiled with 5 per cent. sodium carbonate, and the acids liberated and weighed, gave a yield of 24 per cent. Calculating a 93 per cent. yield of acids for manila, 6 per cent. for kauri, and 2½ per cent. for dammar would require a yield of acids amounting to 26·5 per cent. The application of the alcohol-benzene-carbon disulphide method is as follows:—One to 3 g. is treated with benzene-alcohol (1 : 3), and the white insoluble residue after washing three times with benzene-alcohol is extracted with carbon disulphide. After the evaporation of the alcohol-benzene and of the carbon disulphide, and weighing the extracts, figures are obtained from which the percentages of the three resins present can be derived. The analytical results obtained by Ingle from mixtures of known composition are quite satisfactory.

Synthetic Resins.—The number of synthetic resins is increasing yearly, and reference to *Synthetic Resins and their Plastics* by Carleton Ellis (1923), and *Natural and Synthetic Resins*, Barry, Drummond, and Morrell (1926), will show their increasing importance. It is impossible to refer to the many classes of synthetic resins, but two may be mentioned:—

Phenol-formaldehyde Resins. When phenols and formaldehyde (formalin) are heated in the presence of condensing agents, substances are obtained which resemble varnish resins in appearance and properties. The condensing agent may be an acid, an alkali, or ammonia. The investigation of these substances has been developed by Baekeland and his collaborators. The chief representative of this class is Bakelite, which is manufactured in a number of forms, each with important properties. In place of formaldehyde, benzaldehyde or furfuraldehyde may be used. Resins of the Bakelite type, after fusion with rosin or rosin glyceride, are soluble in drying oils and varnish solvents (Albertols). Steinitzer[1] states that when they are boiled with caustic soda or heated with soda lime, the phenols liberated may be identified by their colour reactions. An improvement on this method has been introduced by Herzog[2] who obtained better results by distilling the powdered sample in a current of nitrogen. The following figures show the amount of phenol obtained from various German products:—

Invelith (Pollak) . . .	17·8 per cent.
Resan (Resanwerke) . .	20·5 "
Dekerit (Raschig) . . .	24·2 "
Faturan (Traun) . . .	21·7 "

[1] *Kunststoffe*, 1915, 5, 109. [2] *Z. angew. Chem.* 1921, 34, Aufsatzteil 97.

The identification of the phenol-aldehyde resins by heating with soda lime to give the phenol component is satisfactory in distinguishing this class of resins from resins of the cumarole and indene group, but it is not characteristic, because Japan lac will yield a phenol; Japan lac, however, is not soluble in methylated spirit. In a resin of the Albertol section the identification of the rosin by the usual method, and of the phenol by heating with soda lime, will be sufficiently characteristic. A small quantity of the powdered resin moistened with cold concentrated sulphuric acid gives a red coloration due to phenols. Colophony gives no coloration.[1] In the examination of phenol-formaldehyde resins, solubility in volatile solvents and the behaviour of the solutions and films therefrom at 70° to 100° are observed, as well as the result of mixing pigments with thin resin solutions, because many of these resin solutions thicken with pigments.

Cumarone Resins. A new class of artificial resins, the cumarone resins, has attracted attention lately. They are polymerisation products of cumarone and indene, obtained from coal-tar naphtha distilling between 160° to 185°, by the action of sulphuric acid. The details of the preparation of cumarone and indene resins by polymerisation are given by Barrett.[2] In the identification of cumarone resins the following characteristics are of value:—Cumarone resins[3] dissolve completely or almost completely in acetone, whilst coal-tar pitch, lignite pitch, wood-tar and petroleum pitch are practically insoluble. Phenol aldehyde resins are insoluble in petroleum, while cumarone resins are partially soluble. The latter also yield only traces of phenols when heated with soda-lime. Natural resins generally melt at a higher temperature, and, with the exception of pontianac resin, have a higher acid number, and higher iodine and saponification values, besides being optically active. Cumarone resins are unsaponifiable by alkali, so that they can easily be separated from drying oils. The final identification of the resin can be effected by fractional distillation of the distillate obtained by heating the resin to 300° to 400°. The largest fraction of the second distillate boils below 160° to 180° (cumarone boils at 172°). Natural resins such as pontianac give a smaller fraction, boiling between 160° to 180°. The presence of cumarone and indene in the distillate can be confirmed by the picrates and bromides (cumarone picrate, m.pt. 102° to 103°; cumarone monobromide, m.pt. 39°; dibromide, 86°; indene picrate, m.pt. 179° to 180°; and indene dibromide, m.pt. 43° to 45°).

A more rapid method of distinguishing between cumarone resin and pontianac is by a colour reaction with bromine.[4] One c.c. of a

[1] Private communication from Mr A. A. Drummond. [2] B. P. 149982, 1920.

[3] Marcusson, *J. Soc. Chem. Ind.*, 1919, 38, 329A.

[4] Wolff, *Farben Zeit.*, 1918, 23, 307.

10 per cent. solution of the resin in chloroform is treated with 1 c.c. of glacial acetic acid and 6 c.c. chloroform, and after shaking, 1 c.c. of a 10 per cent. bromine in chloroform is added and the mixture allowed to stand. Cumarone resin gives a red coloration, which after twenty-four hours is dark red in colour. Pontianac resin gives under the same conditions a yellow orange solution which changes to a yellow colour in twenty-four hours. The presence of 10 per cent. of cumarone resin in pontianac resin will give an orange-red coloration which is permanent after twenty-four hours.

OIL VARNISHES.

The status of oil varnish analysis is not good, and in the opinion of Pearce[1] it is doubtful whether it gives any idea of the comparative practical values of any two samples of varnishes, because it is so difficult to identify the component resins and the state of the oil present in the mixings. The determinations which are usually made comprise those of thinners, resins, oil, and driers. For controlling the products in the factory the tests include specific gravity, viscosity, flash point, colour comparison, drying tests on glass or on a prepared wooden panel, and the examination of the hardness of the film and of its rubbing properties, as well as the action of hot and cold water. The dependence of the properties of the varnish film upon the composition of the varnish as indicated by analytical results is by no means certain, owing to the difficulty in estimating the proportion of resin to thick oil and the want of connection between the properties of the separated resins and the physical and chemical constants of the sweated gum. The separation and estimation of thinners is comparatively simple and accurate (*cf.* pp. 582 *et seq.*). Pearce (*loc. cit.*) has examined the methods for the analysis of oil varnishes put forward by Boughton, Darner, Twitchell, and Scott, and finds that of the first named to be the best. Before giving the details of Boughton's method it is advisable to indicate the principles involved.

The separation of resin acids from fatty acids depends on the comparatively rapid esterification of the latter, so that it is possible to remove the resin acids from the oil esters by means of dilute alkali. Provision has to be made for the separation of the unsaponifiable components of the resin, and for the oxidation products of the oil acids. The details of the method are complicated, and probably Pearce's modification of Boughton's method is the most convenient.[2]

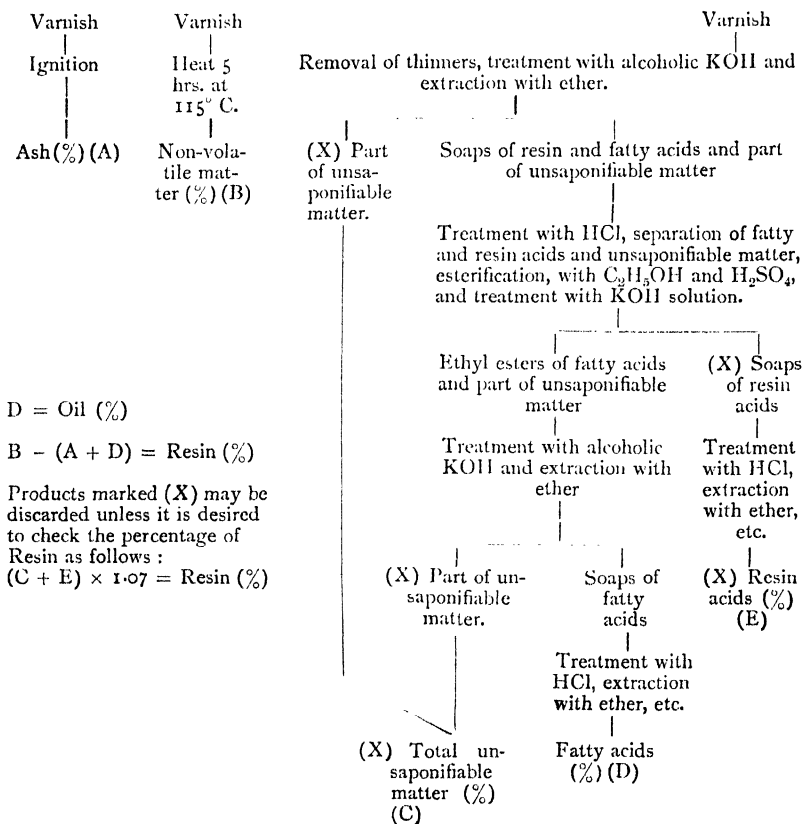
From 4 to 6 g. of varnish is weighed into a 125 c.c. Erlenmeyer flask, 25 c.c. of water added, and the mixture boiled over a very

[1] *Ind. Eng. Chem.*, 1919, 11, 200. [2] W. T. Pearce, *ibid.*, 1920, 12, 552.

small flame until only a few c.c. of water remain. After the removal of the volatile thinners in this way 25 c.c. each of $N/2$ alcoholic potash and benzene are added, and the mixture refluxed for one hour. The solution is evaporated to about 10 c.c. and transferred to a 500 c.c. separating funnel, washing the flask with alcohol, water, and ether. The use of ice-cold ether and ice-cold water is recommended, and very small quantities of alcohol are added when required to break up an emulsion. Water and ether, 100 c.c. of each, are added, and the mixture well shaken. The shaking is repeated three times. The ether layer is washed well with water and separated. A weighed Erlenmeyer flask labelled "Gums" is used to receive this ether layer from the separating funnel. The flask containing the first part of resins (C_1) separated from the other constituents is set aside and used only to receive the ether extracts of resins or unsaponifiable matter (C+E). The unsaponifiable part contains bitumens, if present in the sample.

The aqueous layer and washings[1] are acidified with hydrochloric acid, completely extracted with ether, and the ether separated by distillation from the fatty and resin acids, and the remainder of unsaponifiable matter. To the flask are added 20 c.c. of absolute alcohol, and 20 c.c. of a mixture of four parts of absolute alcohol and one part of concentrated sulphuric acid, and the contents heated with a reflux condenser for five minutes. (The writer recommends heating for one hour.) The mixture is shaken in a separating funnel with 100 c.c. of ether and 100 c.c. of a 10 per cent. solution of sodium chloride. The ether layer is separated and washed with water, and the aqueous layer and the washings of the ether layer are extracted with 50 c.c. of ether. The combined ether extracts (the aqueous layer is discarded) are treated with 50 c.c. of $N/5$ aqueous potassium hydroxide and 10 c.c. of alcohol, and well shaken at least twice after the layers have separated. The ether layer is treated with 50 c.c. of water containing 5 c.c. of $N/5$ potassium hydroxide and 5 c.c. of alcohol, and after settling, the aqueous layer is combined with the original one. These layers are extracted completely with ether and all the ether layers combined and washed. The aqueous portion is acidified with hydrochloric acid, the resin acids (E) extracted with ether, transferred to the flask labelled "Gums" and the solvent distilled off. The ether layers are transferred to the flask and the solvent removed as before. The residue is refluxed with 25 c.c. of $N/2$ alcoholic potash for one hour, and the last of the unsaponifiable matter (C) removed by two or more extractions with 50 c.c. portions of ether. The extracts are added to the "Gums" flask, the solvent

[1] The aqueous solution should be tested for phenols (from synthetic resins) by acidifying and boiling to detect an odour of phenol.

removed and the contents (C+E) dried on a steam-bath overnight and heated to constant weight in a drying oven at 110° to 120°. The aqueous layer containing the fatty acids is acidified as before, completely extracted with ether,[1] and the ether layers washed with water. The ether layer is transferred to a weighed flask and the solvent removed. This flask and contents is heated on a steam-bath overnight, or until all the water is removed, and then heated in the oven to constant weight (D). The following diagram illustrates the method used.

The following results indicate the accuracy of the method. Much depends on the proper degree of esterification. If the esterification

[1] If petroleum ether is used the oxidised fatty acids will remain undissolved and may be collected separately. It is advisable in the analysis of enamels to remove the oxidised oil acids at this stage.

is incomplete the resin values are too high, if overdone then the resin percentage is too low.

	Found.	Calculated.
Thinners	37·1	41·1
Oil	44·9	41·8
Resin	15·6	16·2
	97·6	99·1

A rapid and approximate method of separation of resins and oil may be made by extraction with a large excess of petroleum spirit. Many of the resins are insoluble in petroleum spirit, or only partly soluble, but dammar and rosin and softer gums in the presence of oil dissolve to a great extent. The method is rough and may be misleading unless it be remembered that petroleum spirit fails to extract all the oil and that some of the gums alone or in presence of the oil may dissolve.

Three to five g. of the varnish are weighed into a 250 c.c. beaker, petroleum spirit is added and the varnish is thoroughly stirred until it is well mixed with the spirit. More petroleum spirit is added until the beaker is nearly full and the mixture is again stirred. The beaker is placed in crushed ice and allowed to stand for an hour, when the solution is decanted through a tared filter retaining as much gum as possible in the beaker. More spirit is added and the residue well stirred, the supernatant liquid being again decanted through the filter. The operation should be conducted at 0°, or at a lower temperature if possible. The extraction is repeated with smaller quantities of ether until the residue is as free as possible from oil. The beaker and the tared filter are then dried in the oven and weighed, while the petroleum ether solution of the oil is distilled in a tared flask, preferably in a current of carbon dioxide or nitrogen and the residue weighed.[1]

The following table gives the characteristics of rosin and kauri separated from an oil varnish by Boughton's method.

Varnish.	Saponification Value.	Acid Value.	Ester Value.
From straight rosin varnish	182-185	160-162	22-24
„ ¼ rosin, ¾ kauri „	122-135	44-62	72-78
„ ½ „ ½ „ „	143	88	55
„ kauri varnish	130	45	85
Untreated kauri resin	124	41	83
„ rosin	165-180	155-170	13

The identification of the gums separated from the oil in the above scheme of analysis is uncertain. The determination of the

[1] Fox and Bowles, *loc. cit.*

acidity and iodine value may furnish indications of the presence of a hard or soft copal resin in the varnish.

The resins separated by petroleum spirit may be tested for rosin and other resins by the Halphen-Hicks[1] reaction. The gum is dissolved in a small quantity of carbon tetrachloride and mixed with a few drops of a solution of phenol in carbon tetrachloride (1 vol. phenol: 2 vols. carbon tetrachloride). A drop of the liquid is placed on a white tile and a ring of bromine in carbon tetrachloride (1 vol. bromine: 3 or 4 carbon tetrachloride) is run round the drop but not touching it. The bromine vapour is taken up by the gum solution and produces a more or less characteristic colour change, which may last as long as ten minutes under favourable conditions. Some of the colour changes vary slightly with different samples of gum resin, and may be modified considerably when the gum has been "run," but generally they are fairly reliable. When applying the test it is advisable to make a similar test with the gum or resin whose presence is expected. It is very important to heat a sample of the resin on a piece of tin plate and to notice the odour of the fumes from the heated gum. Shellac, copals and other resins have characteristic odours. The method proposed by K. Brauer[2] for distinguishing between various resins by colour reactions with ammonium phosphomolybdate is not considered by E. Fonrobert and K. Pistor to be sufficiently selective.

Colour Changes in the Halphen-Hicks Test.[3]

Resin.	Colour.
Colophony	Green, rapidly changing to blue and violet; the latter lasts for a time and then changes to purple and indigo blue.
Dammar	Brown, changing slowly to lilac brown; gradually changes to maroon.
Elemi	Immediate indigo blue; sometimes gradually deepens to purple, but generally remains indigo.
Kauri	Azure blue, changing rapidly to purple. The parts furthest from the bromine tend to be dark green.
Manila (spirit soluble)	Slowly forming faint brownish green; changes gradually to violet and finally purple.
Mastic	Reddish brown and carmine near the bromine; coffee brown tint farthest from the bromine.
Sandarac	Persistent lilac almost immediately; gradually changes to violet and violet brown farthest from the bromine.
Shellac	No colour when pure, but faint brown occasionally.
Zanzibar Copal	Light brown forms slowly, becoming brownish violet or chocolate brown with some violet.

[1] *Ind. Eng. Chem.*, 1911, 3, 88.
[2] *Chem. Zeit.*, 1926, 50, 371.
[3] Fox and Bowles, *loc. cit.*, p. 161.

A high percentage of unsaponifiable matter indicates the presence of dammar. The identification of the fatty acids separated from the resin is likewise difficult. Wolff[1] determines the index of refraction of the fatty acids to identify China wood oil in the mixture. The octobromide test may be used for the detection of menhaden oil in the mixture. De Waele[2] describes a method differing only slightly from Boughton's method, in which only the resin is determined and the percentage of oil is obtained by difference, after a direct determination of the thinners. For the details of the method the original paper must be consulted.

J. N. Goldsmith's method (p. 579) may be used and the concentrated petroleum extract examined. The elaidin may be collected, dried in coal gas and weighed (Fox and Bowles, *loc. cit.*, p. 168).

Detection and Estimation of Metallic Driers in Varnishes.

The chief metals to be detected are lead, manganese, cobalt, and calcium. Small quantities of zinc and iron are often found in varnishes in addition to magnesium and phosphates, the two last being components of oil mucilage. Generally the examination is restricted to the detection of lead, manganese, cobalt, and calcium. The ordinary tests and methods of estimation may be performed on the ash obtained on incineration of the varnish. Nevertheless for qualitative purposes there is great saving of time if the varnish can be treated directly with reagents which will detect these metals.[3]

Lead. The varnish is diluted with an equal quantity of light petroleum, and shaken for two minutes with a dilute solution of potassium bichromate. If lead is present, there is no sharp line of division between the two liquids, owing to a precipitate of lead chromate at the dividing surface and on the walls of the test-tube. If the contents of the tube are carefully poured away the lead chromate is found to stick to the glass. The test can be applied in the presence of manganese and cobalt.

Manganese. The presence of manganese or cobalt can be detected without incineration of the varnish by the following method.

The varnish is diluted with an equal volume of light petroleum, a little water and a few drops of potassium hydroxide are added, and the mixture well shaken. Some of the water layer is withdrawn with a pipette and tested with a solution of benzidine in acetic acid. A blue coloration denotes the presence of either manganese or cobalt. In the presence of cobalt it is advisable to incinerate the varnish, treat with hot hydrochloric acid, filter, and neutralise carefully with sodium hydroxide solution. It is best to warm the solution before

[1] *Farben-Zeit.*, 1916, 1302. [2] *J. Oil and Col. Chem. Assoc.*, 1920, 3, 75.
[3] H. Vollmann, *Farben-Zeit.*, 1922, 27, 1943.

the addition of the alkali, but the excess of alkali must only be removed when the solution is cold. If manganese is present, a red colour is produced on the addition of a solution of potassium oxalate, which is said to be due to the formation of $K_3Mn(C_2O_4)_3 \cdot 3H_2O$. It is stated that 0·012 mgrm. of manganese can be detected in 10 c.c. of solution even in the presence of lead and cobalt.[1]

Manganese may be estimated by the usual method in the ash of the varnish. Details of the bismuthate method are as follows:—200 g. of the varnish is incinerated and the ash boiled with nitric acid (sp. gr. 1·2), and during the boiling sodium bismuthate is added, a little at a time, until the permanganate colour persists, indicating that the unextracted oil has been oxidised to the fullest extent. Sulphurous acid is added drop by drop until the permanganate colour disappears and the liquid is then boiled to expel the excess of sulphur dioxide. When this is complete, the solution is cooled thoroughly, about 2 g. of sodium bismuthate added, stirred for about a minute and filtered rapidly through asbestos at the pump. An excess of $N/20$ ferrous ammonium sulphate is added to the cold filtrate. The excess of iron is determined by titration with $N/20$ potassium permanganate. The number of c.c. of $N/20$ ferrous ammonium sulphate used by the manganese divided by 20 gives the percentage of manganese in the extracted pigment.[2]

Cobalt. As in the detection of manganese, the varnish may be examined directly or it may be incinerated and the ash tested. If the varnish is diluted with petroleum or benzene, and shaken with a weak lemon yellow coloured solution of α-nitroso-β-naphthol in glacial acetic acid, a red colour is produced when cobalt is present. If β-nitroso α-naphthol is used the reaction is more sensitive. If the varnish is incinerated and the ash dissolved in a mineral acid, the addition of ammonium sulphocyanate in excess, with a little concentrated potassium acetate and two or three drops of saturated tartaric acid (to remove ferric sulphocyanate), will give a blue coloration in the presence of cobalt due to the formation of $Co(CNS)_4(NH_4)_2$.[3]

Cobalt may be separated from iron and chromium by the acetate separation, and precipitated by means of nitroso-β-naphthol from hydrochloric acid solution (*cf.* pp. 7, 326).

BLACK BITUMINOUS PAINTS AND VARNISHES.

In the analysis of black paints and varnishes the identification of the bituminous components is very difficult. The pitches present may be asphaltums, petroleum pitches, stearine pitches, bone pitches, coal-tar pitches and wood-tar pitches. The asphaltums are usually unsaponifiable, have a brown to brownish black streak, are soluble in white

[1] J. Sacher, *Farben-Zeit.*, 1920, **25**, 1309. [2] Fox and Bowles, *loc. cit.*, p. 140.
[3] P. Slawik, *Chem. Zeit.*, 1914, p. 514; Bellucci, *Gazz. Chim. Ital.*, 1920, **49**, II., 294.

spirit and have a fixed carbon content of 15 to 20 per cent. Petroleum pitches (including blown varieties) are unsaponifiable, neutral and of low iodine value, and are soluble in white spirit. Stearine pitches contain saponifiable matter up to 65 per cent., often with considerable acid and iodine values. They are fairly black in colour and those derived from drying and semi-drying oils are partly soluble in white spirit, whereas those obtained from hard and elastic cotton-seed oils are insoluble. They contain 5 to 10 per cent. of fixed carbon. Bone pitches are intensely black, and contain 15 per cent. of saponifiable matter; they are only slightly soluble in petroleum thinners, and have a fixed carbon content of 20 to 25 per cent. Coal-tar pitches contain free carbon, are unsaponifiable and insoluble in white spirit, but soluble in benzene hydrocarbons.[1] The wood-tar pitches are insoluble in white spirit, unsaponifiable, partially soluble in benzol and insoluble in white spirit. Stockholm tar pitch is easily soluble in alkali owing to the presence of phenolic derivatives, *e.g.* methyl esters of the cresols and of trihydric phenols.

The following tables (V., VI. and VII.) show the characteristics of typical members of the class of bituminous substances.

Table V.

Asphaltites.	Streak.	Sp. gr. at 77° F.	Fusibility.	Percentage Solubility in 88° Naphtha.	Percentage of Saturated Hydro-carbons.	Percentage of Fixed Carbon.
Gilsonite . . .	Brown	1·05-1·10	120°-177° C.	40-60	5·5	10-20
Grahamite . . .	Black	1·15-1·20	177°-315° C.	0·5	0·3	20-30
Glance pitch or manjak .	Black	1·10-1·15	121°-177° C.	20-50	...	20-30
Bermudez asphalt. .	Brown to black	0·95-1·12	15°-162° C.	25-95	24·4	...
Impsonite . . .	Black	1·10-1·25	Infusible	Trace	Trace	...

Table VI.

Petroleum Pitches.	Sp. gr.	Flash Point.	Ash.	Fixed Carbon.	Solubility in Carbon Bisulphide.	Solubility in Naphtha.	Saturated Hydro-carbons.
Californian pitch . (No sulphur)	1·03-1·27	40°-104° C.	0·05-1	12·37	98·6-99	55-82	30
Mexican pitch . (Contains 4·6 per cent. sulphur)	1·015	60°-71° C.	0·05-2	29·32	97·5-98	62-76	30-40
Trinidad petroleum pitch . . . (2·2-2·8 sulphur)	1·15-1·20	55°-99° C.	0·5-1·28	29·38	99·3	66-78	24-38

[1] Coal-tar pitches, lignite and wood-tar pitches containing phenols, when extracted with acetone, give a red coloration with diazobenzene chloride. On evaporation of the acetone extract and boiling the residue with $N/1$ sodium hydroxide and filtering, the filtrate is treated with a few drops of a freshly prepared ice-cold solution of diazobenzene chloride.

Table VII.

	Flash Point.	Insolubility in Benzene.	Percentage of Sulphur.	Iodine Value.
Lignite pitch . . .	86° C.	0	2·14	93·7
Coal-tar pitch . . .	91-92° C.	46	0·31	50·0
Wood-tar pitch. . .	195° C.	42	0·0	140·0
Wool-tar pitch . . .	32° C.	0	0·0	36·9
Stearine pitch . . .	43° C.	0	0·67	40·4
Petroleum pitch . .	126° C.	4	1·00	103·5

The fixed carbon of a pitch is determined by heating 1 g. of the sample in a platinum crucible with a tightly fitting cover for seven minutes over a Bunsen flame, 20 cm. high, the mouth of the burner being 6 to 8 cm. below the bottom of the crucible. The test should be made in a place free from draught. The crucible is cooled and then weighed, the cover is removed and the crucible ignited until only ash remains. Any carbon on the lid is also burnt off. The weight of the residue minus the weight of the ash gives the weight of the fixed carbon. If the ash contains carbonates it is treated with ammonium carbonate and heated for a few minutes before it is weighed. If the tar contains much free carbon, as in coal tars, the free carbon can be determined by extraction of the pitch with hot toluene-benzene, whereby the free carbon present remains undissolved.[1]

Mansbridge [2] gives a scheme for examination and identification of pitches, which, however, does not apply to mixtures. It relies on a division into saponifiable and unsaponifiable bituminous substances, and on the solvent action of white spirit on the members of the two divisions. In section (1) the pitches wholly or partly saponified include stearine and wool grease pitches and bone pitch. (Some stearine pitches, however, are unsaponifiable.) In section (2) the pitches which are unsaponifiable include the natural asphaltums, pitches of the coal-tar and mineral oil group and wood-tar pitch. The solubility of the pitches of section (1) in white spirit may be given as follows:[3] completely soluble in white spirit are the stearine pitches from non-drying fats and wool grease pitch, containing cholesterol: pitches partially soluble in white spirit include the pitches from drying and semi-drying oils and bone pitch. Insoluble in white spirit are the hard and elastic cotton-seed pitches, "rubber pitches." The pitches of section (2) soluble in white spirit comprise the natural asphaltums and soft mineral oil pitches. Partly soluble in white spirit

[1] Cary-Curr, *Ind. Eng. Chem.*, 1912, 4, 535.
[2] *J. Soc. Chem. Ind.*, 1918, **37**, 182T.
[3] The solubility is estimated by boiling about 0·6 g. in 10 c.c. of white spirit, allowing to settle for a few minutes and examining the residue.

are the mineral oil pitches, Trinidad and natural asphaltums containing mineral matter, and ozokerite pitch. Insoluble in white spirit and also unsaponifiable are wood-tar pitch, a few mineral oil pitches giving an asphaltum smell when heated, and coal-tar pitches.

The Analysis of Bituminous Varnishes and Paints.—In Boughton's scheme (p. 604) of varnish analysis the asphaltic pitches will be found in the primary unsaponifiable matter, together with part of the stearine pitch material. The saponifiable part of the stearine pitches will be found in the fatty oils and acids, whereas the resin pitches will appear in the resin acids portion. It is evident that the presence of copals and resins will make the interpretation of the results very difficult; nevertheless, it is possible to form a fair opinion of the amount of the components, if the examination proceeds according to the following scheme.[1]

Bituminous paints, cements, varnishes, enamels and japans may be divided into two general classes, viz.:—

(1) Pigment or filler absent, including bituminous varnishes and japans, also certain bituminous paints and cements.

(2) Pigment or filler present; including bituminous enamels, also certain bituminous paints and cements.

The first class consists of a vehicle made up of a solvent and a base. The second consists of a pigment or filter combined with a vehicle, the latter being made up of a solvent and base. In making an analysis of the paint, cement, varnish, enamel or japan, (1) solvent, (2) pigment or filler, (3) base are separated and examined. The estimation of the solvent may be carried out according to the methods previously described.

Examination of Pigment and Filler in a Bituminous Varnish. One hundred g. of well-mixed material is diluted with 500 c.c. benzene in an 800 c.c. stoppered flask and allowed to stand in a warm place until the pigment or filler is settled. The supernatant liquid is then decanted into a clean flask of large capacity. The pigment or filler is shaken up with 250 c.c. more benzene and allowed to stand in a warm place until it settles, and the supernatant liquid is decanted into the second flask. The treatment with benzene is repeated until the vehicle has been completely extracted from the pigment, and the extracts decanted through a weighed Gooch crucible provided with an asbestos filter. The residues in the flask and in the Gooch crucible are washed with benzene as before, and combined with the balance of the pigment or filler, which is dried at 110° and weighed. The pigment or filler will contain any free carbon black or coal-tar pitch carbon. The benzene extracts are evaporated at 110° preferably in an atmosphere of coal gas to exactly the calculated weight of the

[1] Abraham, *Asphalts ana Allied Substances*, 1918, p. 571.

base, by subtracting the weights of the solvent and the pigment or filler from the original solution of material taken for examination, The base is then examined as follows:—Fifty g. is dissolved in 150 g. of benzene, 10 c.c. dilute nitric acid (1 : 1) added, and the mixture boiled under reflux for half an hour to decompose metallic soaps (driers). One hundred and fifty c.c. water is added, and the liquid again boiled under reflux to remove the nitrates of metallic driers. The extraction with hot water is repeated and the benzene solution of oils, pitches, and resins separated. The benzene solution is distilled to 100 c.c. bulk, and boiled under reflux with 300 c.c. of a 10 per cent. alcoholic potash solution (100 g. caustic potash, 500 c.c. 95 per cent. alcohol, and diluted with 90 per cent. benzene to a litre) for one hour, and the unsaponifiable matter separated. The unsaponifiable matter may contain sterols together with the unsaponifiable constituents of the resins (amounting to 4 to 8 per cent. of the resins present), and the unsaponifiable components of the pitches, *e.g.* asphalt, coal-tar pitch and unsaponifiable matter from stearine pitches. The saponifiable matter is dealt with under the scheme of varnish analysis already given (p. 604). The difficulties of distinguishing between the fatty acids derived from the vegetable oils and those from the fatty pitches which may be present are very great. The following differences may be considered as a guide only:—

	Fatty Acids from Oils.	Fatty Acids from Pitches.
Lactone value . . .	less than 25	greater than 25
Kramer-Sarnow fusion point .	„ „ 80° C.	„ „ 80° C.
Hardness at 77° F. (Consistometer)	„ „ 5	„ „ 5
Colour in mass . . .	Translucent yellow to brown.	Opaque brown to black.

The United States Government Specification for Asphalt Varnish[1] requires that the varnish shall be composed of a high grade of asphalt fluxed and blended with properly treated drying oil and thinned to the proper consistency with a volatile solvent. It must be resistant to air, lubricating oil, water, and when the contract so specifies, to mineral acids of the concentration herein specified. It must meet the following requirements:—

Appearance.—Smooth and homogeneous; no livering and stringiness.

Colour.—Jet black.

Flash Point.—Not below 86° F.

Action with Linseed Oil.—Varnish must mix readily to a homogeneous mixture with an equal volume of raw linseed oil.

Matter Insoluble in Carbon Disulphide.—Not more than 1 per cent.

Non-volatile Matter.—Not less than 40 per cent. by weight.

[1] *Circ. Bureau of Standards*, 1923, 104.

Fatty Matter.—Not less than 20 per cent. of the non-volatile. Must be liquid and not show a violet coloration by the Liebermann-Storch test.

Set to touch.—Within five hours.

Dry hard and tough.—Within twenty-four hours.

Toughness.—Film on metal must withstand rapid bending over a rod 3 mm. ($\frac{1}{8}$ in.) in diameter.

Working Properties.—Varnish must have good brushing, flowing, covering and levelling properties.

Resistance to Water.—Dried film must withstand cold water for eighteen hours.

Resistance to Mineral Acids.—Dried film must withstand action of the following acids for six hours—sulphuric acid, sp. gr. 1.25; nitric acid, sp. gr. 1.12; hydrochloric acid, sp. gr. 1.09.

The details of the majority of these requirements have already been discussed; the method of determination of the fatty matter is as follows:—

About 5 g. of the varnish is weighed into a wide-mouthed flask, 5 g. of clean dry sand and 50 c.c. of benzene added and the mixture heated under a reflux condenser on the water bath until the varnish is dissolved. It is then saponified for half an hour with 50 c.c. of $N/4$ alcoholic caustic soda, and the mixture evaporated to dryness. The residue is heated with 50 c.c. of water until it is disintegrated, the liquid filtered and the residue extracted with boiling water until the washings are colourless. The aqueous extract is acidified with hydrochloric acid and heated until the fatty acids and any emulsified asphalt separate, cooled and extracted several times with ether in a separating funnel. The ether extracts are washed to remove acid and evaporated to dryness. The residue is taken up in 95 per cent. alcohol, filtered, evaporated to dryness, dried at 105° and the fatty acids weighed and returned as fatty matter.

Abraham[1] describes a method for the examination of the dry films of paints, cements, varnishes, enamels and japans which has been found to yield fairly accurate results:—50 g. scrapings are boiled with 350 c.c. of the special saponifying agent (p. 614) under a reflux condenser for one hour. 300 c.c. benzene-alcohol (1 : 1) is added, the liquid boiled, allowed to settle and the supernatant liquid decanted into a large flask. The extraction is repeated until complete and the extracts then combined and allowed to stand to recover any further settlings. The residue is dried at 100°, pulverised and extracted in a Soxhlet for twelve hours with benzene-alcohol (2 : 1). The residue, which includes pigments and fillers, free carbon from tars or pitches, also any metallic driers, is dried, ignited and weighed. The two benzene-alcohol extracts are combined, evaporated to a small bulk and examined as under the scheme for varnish analysis previously described (p. 604).

[1] *Loc. cit.*, p. 573.

Cellulose Ester Varnishes and Enamels.

No comprehensive scheme for the analysis of cellulose ester varnishes and enamels has yet been devised. Much depends on the skill of the analyst in obtaining clues as to the ingredients present and methods must be devised to suit the particular mixtures under examination. The separation, identification and quantitative estimation of mixtures of organic solvents are very difficult without a previous knowledge of all the ingredients present.

D. B. Keyes[1] and A. E. Lain[2] have given a valuable summary of the principal ingredients of cellulose nitrate lacquers.

Sproxton[3] states that more can be learnt about a sample in a short time by close observation of its behaviour as a film and its odour, together with its price, than can be learnt in the same time from its chemical behaviour. Nevertheless certain methods are available and yield results which are of considerable assistance.

Dabisch[4] has put forward schemes of analysis of cellulose esters, which he admits are only tentative and incomplete.

H. A. Gardner[5] describes methods of examination of pyroxylin: lacquer coatings.

In judging the probable composition of a cellulose lacquer the determination of the specific gravity, viscosity, lustre or dullness on drying, behaviour upon flowing on glass or spraying on sheet metal, thickness of the film obtained and the odour of the various solvents and thinners will be of assistance in judging the probable composition of a lacquer under examination.

The viscosity may be determined by the falling sphere viscometer as standardised by Gibson and Jacobs.[6] The instrument should be calibrated against a standard material such as glycerine = 100, and the result expressed in absolute C. G. S. units, or in a unit easily convertible thereto. In works' practice the viscosity by the steel ball method is expressed by the number of seconds taken for the ball 2 mm. in diameter (0·032 g.), to fall through 25 cm. of the solution at 18°. A glass cylinder, 3 cm. wide, is used. A modification of this viscometer due to Mardles[7] can be employed for opaque solutions in which a weight is attached to a fine wire on the other end of which is a counterpoise. The wire is hung over a low friction pulley and the weight allowed to fall in the solution. The rate of fall is measured by the rate of rise of the counterpoise. In the B. E. S. A. Specification for

[1] *J. Oil and Col. Chem. Assoc.*, 1925, **8**, 228.
[2] *Ibid.*, 1926, **9**, 33.
[3] *Cellulose Ester Varnishes*, 1925.
[4] *Farben-Zeit.*, 1927, 1609.
[5] *Physical and Chemical Examination of Paints, Varnishes and Colours*, 1925.
[6] *J. Chem. Soc.*, 1920, **117**, 473.
[7] *Trans. Faraday Soc.*, 1923, **18**, 337.

Nitrocellulose Syrup (2 D. 8th Nov., 1921) the Ostwald viscometer is used and determinations compared with glycerine = 100 at 25° are made. For details of the determination of viscosity by the two methods reference should be made to the British Standard method for the determination of viscosity in absolute units, B. E. S. A. Specification, No. 188, 1923.

Much information can be obtained regarding the non-corrosive properties of a clear lacquer, or of solvents to be used therein, by evaporating 5 c.c. in a polished spun copper dish. The evaporation is performed on a steam bath, and the free acid developed from unstable nitrated cotton will cause a green discoloration (Gardner). The free acidity may be determined by adding to the clear lacquer a neutralised mixture of 50 per cent. aqueous alcohol until all the solids are precipitated, and determining the acidity of the clear supernatant liquid by titration with standard alkali (Gardner).

The separation of pigments from an enamel is a very difficult matter owing to the fineness of the pigment particles and the difficulty of obtaining a clear liquid from the highly thinned pigmented lacquer either by allowing to settle or by centrifuging; filtration is impossible. Incineration of a 20 g. sample of the lacquer will leave an ash containing the mineral components of the great variety of pigments. When Prussian blue is present it is necessary to make a nitrogen determination of the residue obtained by evaporation of the lacquer with allowance for the nitrogen content of the nitrocellulose, the amount of which must be determined. When organic colours are present, *e.g.*, paranitraniline, toluidine reds and similar toners, Gardner[1] proposes to precipitate the cotton present with water, whereby the greater part of the pigment is carried down. After removal of the solvent and water the mixture of cotton and pigment can be dried, and the cotton can be largely extracted with a light volatile ester such as ethyl acetate. For the estimation of the total solids the method recommended by Sproxton,[2] is simple. A sample of the lacquer is weighed into a wide-mouthed bottle or sample tin; the rounded bottom of a weighed test tube is dipped into the lacquer solution, and after withdrawal and draining the wide-mouthed bottle or sample tin is weighed again. The difference in weight is the amount transferred to the outside of the tube. The latter is kept in a warm place until free from the smell of solvent, and is then weighed at intervals until a sufficiently constant weight is obtained. The appearance and manner of drying of the film can be very conveniently studied, and the coating easily removed later as a thimble by placing the tube in hot water for a few seconds.

Estimation of the Nitrocellulose.—For a mixture containing nitrocellulose, resin and pigment, amyl acetate, amyl alcohol, methyl alcohol

[1] *Loc. cit.* [2] *Loc. cit.*

and petroleum spirit, Lorenz[1] recommends precipitation of the nitrocellulose with fusel oil. Conley[2] considers that some nitrocellulose remains in the fusel oil solution, and recommends precipitation by the gradual addition of chloroform with continuous shaking. If no resins or pigments are present, the precipitate is pure nitrocellulose, which may be filtered off, dried and weighed. If resins are present in considerable amount, the precipitate of nitrocellulose will be contaminated with resin. It is then necessary to decant the clear liquor as completely as possible, to redissolve the nitrocellulose in the smallest possible quantity of solvent, *e.g.* acetone, and to reprecipitate with chloroform. Sproxton considers that no method of precipitation of nitrocellulose by organic solvents is easy to carry out and recommends precipitation with aqueous electrolytes. A film is first obtained directly from a weighed or measured quantity of the original solution as in the determination of the total solids. The amount of film should be enough to yield about 0·5 g. of nitrocellulose. If oils or resins are present, they are extracted with chloroform or any other appropriate solvent under reflux or in a Soxhlet extractor. If they are not present this step is unnecessary. The film is then dissolved in 50 c.c. of acetone and diluted with aqueous alcohol (50 per cent.). The quantity cannot be stated definitely, since it differs according to the solubility of the nitrocellulose, but it must be sufficient to convert the solution to an opalescent colloidal solution, blue by reflected light and red by transmitted light. Such a solution passes unchanged through filter paper. On adding to it a dilute aqueous solution of an electrolyte, such as 2 per cent. ammonium chloride, it is coagulated to a manageable precipitate. The liquid is boiled, allowed to settle, and filtered through a Gooch crucible and the precipitate dried at 40°. The cellulose nitrate is obtained in a suitable form for examination by the use of this method. The nitrogen content of the nitrocellulose is determined by the ferrous chloride Schultze-Tiemann method.

Dabisch[3] recommends precipitation of the cellulose by petroleum, b.p. 35°-50°, the lacquer being poured into the petroleum spirit. It is advisable to try beforehand what is the amount of petroleum necessary, as it may vary from a small fraction of the sample to 150 per cent. of its bulk. If the precipitate remains colloidal the addition of a small amount of acetic acid is advisable. The liquid is filtered and the filtrate contains the lacquer solvents as well as plasticisers and resins; some of these may be carried down with the cellulose, which will require special treatment. Digestion of the precipitated nitrocellulose with butanol will remove shellac and spirit soluble resins, whereas treatment with benzene or toluene will remove oil soluble resins carried down with the

[1] *J. Amer. Leather Chem. Assoc.*, 1919, 14, 548.
[2] *Ind. Eng. Chem.*, 1915, 7, 882.
[3] *Loc. cit.*

nitrocellulose. It is important that the mass to be extracted should be dry and in the form of a fine powder; it is mixed with sand to make the extraction easy. Treatment of purified cellulose with a solvent of low boiling point will give the cellulose in a form suitable for analysis. The nitrocellulose used in varnish and enamel manufacture contains from 11·7 to 12·2 per cent. of nitrogen.

Examination of Thinners and Plasticisers.—The scheme put forward by Dabisch is more systematic than the schemes of other investigators. He separates the nitrocellulose by precipitation with very light petroleum (b.p. 35° to 50°), and obtains an extract which is fractionated up to 200°. The following is the list of solvents occurring within that range of temperature. He examines the fractions of 20° to 30° for the

Boiling Point.		Specific Gravity	Boiling Point.		Specific Gravity.
Degrees.			Degrees.		
34·6	Diethyl ether	0·720	124	Glycolmonomethylether	0·975
42	Methylene chloride	1·38	124·5	*n*-Butyl acetate	0·890
54·5	Ethyl formate	0·936	125	Diethyl carbonate	0·976
56·5	Acetone	0·792	127	Ethylene chlorhydrin	1·202
57·2	Methyl acetate	0·957	130·6	Isoamyl alcohol	0·824
65	Methanol	0·789	132	Monochlorbenzene	1·112
	Benzine	...	135	Glycolmonoethylether	0·936
77·1	Ethyl acetate	0·904	137-145	Isoamyl acetate	0·878
78·3	Ethyl alcohol	0·800	138-143	Xylene	0·862
From 80 to 120	Fusel Oil Components	...	140	Glycolmonomethylether acetate	1·006
80·5	Benzene	0·879	142·5	*n*-Propyl *n*-butyrate	0·878
From 81 to about 140	Methylethyl ketone and light Acetone Oil	0·813 and above	145	*n*-Butyl propionate	0·880
			150	Glycolmonoethylether acetate	0·976
82·4	Isopropyl alcohol	0·791	155	Ethyl lactate	1·031
87	Isopropyl acetate	0·877	157	Cyclohexanone	0·947
87	Trichloroethylene	1·471	156-162	Chlortoluene	1·074
97·5	*n*-Propyl alcohol	0·807	160	Isoamyl propionate	0·888
99·2	Ethyl propionate	0·896	163	*n*-Butyl *n*-butyrate	0·880
100	Water	1·000	163	Dimethyl oxalate	1·157
102	*n*-Propyl acetate	0·889	164	Diacetone alcohol	0·930
108·4	Isobutyl alcohol	0·803	165-170	Methylcyclohexanone	0·920
110·6	Toluene	0·882	174	Cyclohexanol acetate	0·974
116·1	Isobutyl acetate	0·858	179-194	Methylcyclohexanol acetate	0·945
117	*n*-Butanol	0·810			
119·6	Ethyl *n*-Butyrate	0·902	185	Diethyl oxalate	1·082
122·4	*n*-Propyl propionate	0·880	204·5	Benzyl alcohol	1·041

corresponding solvents[1] given in the table by determination of the water soluble, the sulphuric acid insoluble, water insoluble, and finally the saponification value of the fraction mixture. An example will show the method of procedure. Suppose 26 c.c. of a fraction b.p. 100° to 125° is collected, and 10 c.c. is shaken with 25 c.c. of an aqueous calcium chloride solution. The gain in volume of the aqueous solution is 3·8 c.c., or the water soluble portion in 26 c.c. is 9·9 c.c. Another

[1] For the special methods for estimation of individual solvents reference must be made to those given under their names in other volumes of this work.

10 c.c. of the mixture is shaken with a third of its volume of sulphuric acid (sp. gr. 1·8) and 2·3 c.c. is undissolved by the sulphuric acid, *i.e.* 6 c.c. of the 26 c.c. of the fraction collected.

The saponification value of the remaining 6 c.c. of the fraction is found to be 121, whereas the saponification value of butyl acetate is 484, *i.e.* 25 per cent. of the fraction is butyl acetate. Collecting these results the conclusion drawn is that 6 c.c. consist of toluene and petroleum (insoluble in sulphuric acid), 9·9 c.c. (water soluble) consist of glycolmonomethylether, which is odourless, and 6·5 c.c. of butyl acetate, leaving a residue of 3·6 c.c., which must be butanol, because it is water insoluble, but soluble in sulphuric acid. This is represented by the difference between 26 and the sum of 6 plus 9·9, *i.e.* 10·1, from which 6·5 representing butyl acetate must be subtracted leaving 3·6, representing the amount of butanol given above. A similar treatment of successive fractions and reference to the list of solvents within the given range will enable an approximate composition of the thinners to be found.

The distillation residue will consist of volatile and non-volatile plasticisers and resins. If necessary the precipitated cellulose must be extracted with benzene or toluene to remove oil soluble resins, and once with butanol to remove shellac and spirit soluble resins. The resins present in a cellulose lacquer may include rosin, rosin esters and albertols, which will be found in the distillation residue, and can be detected by the usual tests, together with fused resins, dammar, accaroid, shellac and bakelites, which occur partly in the precipitated cellulose. The detection of the plasticisers in the distillation residue will include the separation of camphor, which is removed by distillation in steam, and estimated by its optical rotation if natural camphor is present; and the saponification of the residue and subsequent acidification whereby resin acids and oil acids (*e.g.* ricinoleic acid from castor oil), insoluble in water, are obtained and estimated as in oil varnish analysis (p. 604). The water soluble acids include phosphoric, phthalic, tartaric, benzoic, acetic and lactic acids, and carbaminic acid as ammonium salt. The alcoholic components of the plasticisers comprise methyl, butyl and amyl alcohols, phenols, glycerine and glycols, which will be found among the products of saponification. The method used depends largely on the nature of the sample, and the accurate estimation of the components is tedious and in some cases impossible.

The following list of plasticisers may be taken as representative, but it is being added to from year to year:—

	Boiling Point.		Boiling Point.
Tricresyl phosphate	>350°	Diamyl phthalate	>340°
Tiphenyl phosphate	>325°	Diethyl tartrate	>300°
Diethyl phthalate	290°	Triacetin	267°
Dibutyl phthalate	340°	Camphor (solid)	209°

Cellulose Acetate Enamels and Lacquers.

The methods of analysis of these products are much simpler, as the range of solvents and plasticisers is more limited, and there is a general absence of resins, because cellulose acetates combine with them with difficulty. The cellulose acetate lacquers consist essentially of solvents, plasticisers and acetylcellulose. Acetylcellulose is more easily precipitated by petroleum ether than nitrocellulose. After filtration and washing with petroleum ether the acetylcellulose may be estimated by its acetic acid content. According to Dabisch[1] the filtrate may be fractionated and examined as described under nitrocellulose lacquers (p. 619). The distillation residue contains plasticisers, and, in exceptional cases, resins. If nitrocellulose is present the acetylcellulose may be precipitated by methyl alcohol, and the filtrate may be examined as a cellulose nitrate lacquer, as nitrocellulose is not precipitated by methyl alcohol. Sproxton suggests the following scheme as a working basis:—

(*a*) The solid content is determined by filming off a weighed quantity of solution. The solid content consists of cellulose acetate and the softeners, such as triphenyl phosphate, triacetin, benzyl alcohol and acetanilide. After extraction of the film with low boiling non-solvents such as ethyl ether, the weight of the cellulose acetate remaining, and its acetyl group content are determined. Resins are not found in cellulose acetate varnishes.

(*b*) Identification of the softener by precipitation of the cellulose acetate by ether and examination of the ethereal solution for organic phosphates.

(*c*) Dry distillation up to 120° followed by steam distillation should give information about the volatile solvents. Tetrachloroethane is not likely to be found in a modern acetate varnish, but is easily recognised by its smell. Fractionation of the dry distillate and miscibility of the fractions should show the presence of benzene, acetone and methylethyl ketone. Quantitative determinations are, according to Sproxton, not likely to be of much use, but a saponification to determine ester (methyl acetate) and an acetylation to determine free hydroxyl (ethyl alcohol and possibly methyl alcohol) may be of value.

[1] *Loc. cit.*

LITERATURE.

H. ABRAHAM.—*Asphalts and Allied Substances*, 1918.

T. H. BARRY, A. A. DRUMMOND and R. S. MORRELL.—*Natural and Synthetic Resins*, 1926.

K. DIETERICH.—*Analysis of Paints*, 2nd Engl. edition, 1920.

J. J. FOX and T. H. BOWLES.—*Analysis of Pigments, Paints and Varnishes*, 1927.

P. J. FRYER and F. E. WESTON.—*Oils, Fats and Waxes*, Vols. I. and II., 2nd edition, 1923.

H. A. GARDNER and J. A. SCHAEFFER.—*Analysis of Paints and Painting Materials*, 1911.

H. A. GARDNER.—*Physical and Chemical Examination of Paints, Varnishes and Colours*, 1925.

N. HEATON.—*Volatile Solvents and Thinners*, 1926.

D. HOLLEY and E. F. LADD.—*Analysis of Mixed Paints, Colour Pigments and Varnishes*, 1908.

H. M. LANGTON.—*Blacks and Pitches*, 1925.

J. LEWKOWITSCH and G. H. WARBURTON.—*Chemical Technology and Analysis of Oils, Fats and Waxes*, 6th edition, 1921.

R. S. MORRELL.—*Varnishes and their Components*, 1923.

R. S. MORRELL.—*The Chemistry of Drying Oils*, 1926.

J. SCHEIBER.—*Lacke und ihre Rohstoffe*, 1926.

F. SEELIGMAN and E. ZIEKE.—*Handbuch der Lack- und Firnis-Industrie*, 3rd edition, 1923.

F. SPROXTON.—*Cellulose Ester Varnishes*, 1925.

H. WOLFF.—*Die Lösungsmittel der Fette, Öle, Wachse u. Harze*, 1922.

Atomic Weights (1925)

	Symbol.	Atomic Weight.		Symbol.	Atomic Weight.
Aluminium	Al	26·97	Molybdenum	Mo	96·0
Antimony	Sb	121·77	Neodymium	Nd	144·27
Argon	Ar	39·91	Neon	Ne	20·2
Arsenic	As	74·96	Nickel	Ni	58·69
Barium	Ba	137·37	Niobium Nb (= Columbium Cb)		93·1
Beryllium Be (= Glucinum Gl)		9·02	Nitrogen	N	14·008
Bismuth	Bi	209·00	Osmium	Os	190·8
Boron	B	10·82	Oxygen	O	16·000
Bromine	Br	79·916	Palladium	Pd	106·7
Cadmium	Cd	112·41	Phosphorus	P	31·027
Caesium	Cs	132·81	Platinum	Pt	195·23
Calcium	Ca	40·07	Potassium	K	39·096
Carbon	C	12·000	Praseodymium	Pr	140·92
Cerium	Ce	140·25	Radium	Ra	225·95
Chlorine	Cl	35·457	Radon	Rn	222·
Chromium	Cr	52·01	Rhodium	Rh	102·91
Cobalt	Co	58·94	Rubidium	Rb	85·44
Copper	Cu	63·57	Ruthenium	Ru	101·7
Dysprosium	Dy	162·52	Samarium	Sa	150·43
Erbium	Er	167·7	Scandium	Sc	45·10
Europium	Eu	152·0	Selenium	Se	79·2
Fluorine	F	19·00	Silicon	Si	28·06
Gadolinium	Gd	157·26	Silver	Ag	107·880
Gallium	Ga	69·72	Sodium	Na	22·997
Germanium	Ge	72·60	Strontium	Sr	87·63
Gold	Au	197·2	Sulphur	S	32·064
Hafnium	Hf	178·6	Tantalum	Ta	181·5
Helium	He	4·00	Tellurium	Te	127·5
Holmium	Ho	163·4	Terbium	Tb	159·2
Hydrogen	H	1·008	Thallium	Tl	204·39
Indium	In	114·8	Thorium	Th	232·15
Iodine	I	126·932	Thulium	Tm	169·4
Iridium	Ir	193·1	Tin	Sn	118·70
Iron	Fe	55·84	Titanium	Ti	48·1
Krypton	Kr	82·9	Tungsten	W	184·0
Lanthanum	La	138·90	Uranium	U	238·17
Lead	Pb	207·20	Vanadium	V	50·96
Lithium	Li	6·940	Xenon	Xe	130·2
Lutecium	Lu	175·0	Ytterbium	Yb	173·6
Magnesium	Mg	24·32	Yttrium	Yt	88·9
Manganese	Mn	54·93	Zinc	Zn	65·38
Mercury	Hg	200·61	Zirconium	Zr	91·

INDEX OF AUTHORS

INDEX OF SUBJECTS

CONTENTS OF VOLS. III-VI

IN PREPARATION

VOLUME III

Subject	Author
Clay Claywares, Earthenwares, and Refractories	H. V. THOMPSON, M.A., and S. R. HIND, B.Sc., A.R.C.S.
Glass	J. D. CAUWOOD, M.Sc., and J. H. DAVIDSON, M.Sc.
Cements	GEOFFREY MARTIN, D.Sc., Ph.D.
Potable Water	Prof. G. J. FOWLER, D.Sc.
Feed Water for Boilers	L. O. NEWTON
Sewage and Effluents	Prof. G. J. FOWLER, D.Sc.
Artificial Manures Feeding Stuffs	BERNARD DYER, D.Sc.
Soils	Sir A. D. HALL, K.C.B., F.R.S.
Air	J. S. OWENS, M.D., A.M.I.C.E., and J. H. COSTE

VOLUME IV

Subject	Author
Illuminating Gas Ammonia, etc.	H. G. COLMAN, D.Sc., Ph.D.
Coal Tar	A. F. CAMPBELL, D.Sc.
Organic Dyes	T. CALLAN, M.Sc., Ph.D.
Explosives	R. C. FARMER, D.Sc., Ph.D.
Calcium Carbide and Acetylene	THOMAS COXON, M.A.
Matches and Fireworks	Prof. J. REILLY, M.A., D.Sc.

VOLUME V

Mineral Oils
Lubricants
Oils, Fats, and Waxes
Vegetable Drugs and Galenicals
Essential Oils and Perfumes
Tartaric and Citric Acids
Fine Chemicals
Synthetic Drugs and Alkaloids
Disinfectants
Vegetable Tanning Materials
Leather
Inks

VOLUME VI

Sugar
Starch and Dextrin
Alcohol, Spirits, and Liqueurs
Brewing Materials and Beer
Wine
Vinegar
Paper
Textiles
Rubber
Glue and Gelatine

PRESS REVIEWS

VOLUME I. (SECOND EDITION)

"Although this manual was originally written in German, it has been influenced to such an extent by British works practice and has been so thoroughly revised by Dr Keane and his collaborators, that it is expressive rather of British than continental practice. The popularity of the first edition of the book is significant for the triumph of scientific methods in British practice of technical analysis. The keen competition with which works in this country have to contend demands accurate analytical methods, a need which will derive much help from this volume. There is frequently a choice of methods available for any desired accuracy and the corresponding expenditure of time. Taken all round, it is a useful book which should find a place in every analytical laboratory."—*Chemical Age* (London), 31st May 1924.

"All chemists concerned with technical analysis are sure to welcome the second edition of this standard treatise, the first volume of which has now left the press. The names of the present editors and their collaborators convey an assurance that the book will fully maintain its reputation for general excellence and comprehensiveness."—Dr W. R. Schoeller in *Chemistry and Industry.*

"The first volume of the new edition of this work, which will be published in six separate volumes, has recently appeared. As stated in the preface, the volume under review contains two new sections, viz., 'Electrolytic Methods of Chemical Analysis' and 'Physical Methods employed in Chemical Analysis.' Of the new sections that on 'Electrolytic Methods of Chemical Analysis' is written by Dr H. J. S. Sand, an original worker and acknowledged authority in this field. In the author's words, 'this section consists of an account of the methods available for electrolytic analysis, of the apparatus employed, and the general conditions applicable to the solutions in which the electrolysis is effected.' This section is a model of brevity and conciseness, and it is hoped that Dr Sand will contribute further sections dealing with individual estimations.

"The section on 'Physical Methods employed in Technical Analysis,' by Dr J. S. G. Thomas, gives an account of many of the more important instruments employed in technical laboratories, and contains a great deal of valuable information which is not readily available to the majority of chemists. No mention is made of the spectrometer but, presumably, this will be included in a later volume. The joint editors deal very fully with 'Technical Gas Analysis,' and the sampling and analysis of fuel is described by Mr G. N. Huntly, who shows a first-hand knowledge of the subject treated. The description of the methods used in the examination of the raw materials, products, and by-products of the acid, alkali and chlorine industries, originally written by the late Dr Lunge, has been revised for this edition by Dr Dunn. In the concluding section Mr H. Williams deals with the detection and estimation of cyanogen compounds in the various commercial products in which these occur. It is stated in the text that the methods selected are those which combine speed with accuracy, and the author appears to have succeeded in making a wise and discriminating choice. 'Lunge' has always been regarded as a standard text-book upon the subject-matter treated, but, with the present additions and revision, the book now becomes practically indispensable to all chemists who are engaged upon the general scope of the work; accuracy of description of methods is carried to a high degree and the new volume is to be recommended as worthy of being on the reference shelves of chemists, manufacturers, and others who have to consider the subject from the technical aspect. The indexing is ample and the references, on the whole, comprehensive."—G. Rudd Thompson, Esq., F.I.C., in the *Analyst.*

VOLUME II. (FIRST EDITION)

"It is needless to say that every analytical chemist and assayer must own these encyclopædic works; especially Volume II. now issued, as it reviews the analytical methods in connection with the metals."—*Mining Magazine.*

"In reviewing the first volume of this work in our issue of December 1908 we referred to the general excellence of the methods of treatment in regard to the various sections."—*The Textile Manufacturer.*

"These two parts form a welcome addition to the two (Volume I.) issued in 1908 and reviewed in this journal. The high character of the earlier issues has been maintained, and the list of names of those who have collaborated with Dr Lunge in writing the German edition, and with Dr Keane in translating it into English, and particularly in adapting it to English requirements, justifies us in stating, as is indeed proved throughout the work that this is not a mere collection of information, but is an authoritative work from which matters of doubtful utility have, so far as possible, been excluded."—*Mining Journal.*

Extracts from Press Notices

We learn from the preface that this translation of Schmidt's "Kurzes Lehrbuch der organischen Chemie" arises from the encouraging results that attended the adoption of the German original as a text-book for the advanced students in the University of Edinburgh, and indeed the translator has done his work so admirably and produced so readable a book that there can be no question that it also will find a similar welcome in other English-speaking Universities. It is the type of book that the teacher can recommend with confidence to the more ambitious second-year and pass students in organic chemistry, and, in so far as any single text-book can meet the ever-growing requirements of the honours students of a university, this book will prove both helpful and useful.—*Nature.*

There can be no question that, by reason of its general arrangement, the clearness with which the fundamental issues are treated and the interesting manner in which the narrative is written, the book will be equally successful in other universities.—*Chemistry and Industry.*

A translation of this excellent book has long been needed. It is a valuable reference work and yet no mere dictionary, for it is thoroughly interesting and readable in every part. The translator has revised the text of the German edition, added much new material, and inserted many references to English and American authors. Schmidt's Organic Chemistry is comprehensive and well suited to advanced students. It is not encumbered with too much detail, but gives broad outlines in an extremely interesting way. The book stimulates thought and, so it appears to the reviewer, has a distinct bias towards that branch of chemistry which probably will be the subject of much research in future years, namely, the chemistry of natural products. The translator has done his work so well that the awkward sentences which characterise the German language have been turned into such lucid English that it is difficult to believe that it is a translation. The publishers too have done their share by producing a well-bound, clearly printed book which deserves a place in every chemical library and can be thoroughly recommended to all advanced students in both chemistry and bio-chemistry.—*The Analyst.*

In preparing the translation, the author has made a few departures from the German original, notably from the point of view of dealing with recent work on the carbohydrates and other natural products, of altering the nomenclature in conformity with the latest international conventions and of extending the references to journal literature with the object of drawing attention to some of the important work carried out by British investigators, and of proving that organic chemistry is not altogether a German science. The treatment of the subject is on conventional lines, but much more attention is given to heterocyclic compounds than is generally the case. This undoubtedly enhances the value of the book to the student. The sections on alkaloids and proteins and on chlorophyll and other plant pigments are particularly worthy of mention. The work contains but few obvious typographical errors and would appear to be eminently suitable for the use of students preparing for an honours degree in Chemistry.—*Transactions of the Faraday Society.*

Schmidt's "Kurzes Lehrbuch der organischen Chemie" has already established a reputation for itself in this country, and has been adopted in the German original at some universities as the text-book for advanced students in chemistry. The English edition is particularly well printed and arranged, and Dr Rule is to be congratulated on the successful performance of a difficult and lengthy task. A number of additions and modifications have been made in the English edition, chief among which is the rearrangement of the formulæ for numbering heterocyclic compounds, in accordance with the rules which have recently been provisionally passed by the International Union of Pure and Applied Chemistry. Excellent author and subject indexes enhance the value of a work which should meet with a ready welcome from students of organic chemistry.—*Chemical Trade Journal.*

Extracts from Press Notices

Having spent no inconsiderable part of a pleasant vacation in reading this book, the reviewer has formed the opinion that the only adequate method of reviewing it is simply to issue an order that it be read by all chemists. It is difficult in a review to convey a just appreciation of its peculiar merits, but it is necessary to observe the conventions, so we proceed as follows. Many authorities have warmly commended the original German work on which this translation is based, and Mr Thorne has done British chemists a material service in rendering the book readily available to them. It is unique in plan, and its scheme is carried out in an admirably thorough and painstaking manner. The book is remarkable for the great amount of material it contains, for the orderly arrangement of that material, and for the success the author has achieved in systematising the data. It is, perhaps, desirable to emphasise the fact that this is a text-book for the use of those who have a fair working knowledge of chemistry: it would be quite unintelligible to the beginner, and its real use and merit is as a text-book and work of reference for advanced students and practising chemists. To such it presents a coherent, orderly and unusually complete statement of inorganic chemistry. The book makes slow yet pleasant reading: slow because it is so closely packed with material, pleasant because both facts and theories are stated simply, clearly, and in order. Here much praise is due to the translator, who has faithfully given the whole substance of the original, with much additional matter, in good readable English. It is not translated German. The book is well printed on good paper and well bound. It should be owned and read by every chemist.—H. V. A. BRISCOE, *Chemistry and Industry.*

Professor Ephraim's book is arranged on a plan which, whilst unsuited to the needs of elementary students, makes it very valuable both as a text-book for students who already have a fair knowledge of the subject and as a work of reference. It contains a surprising amount of detail for its size, yet it is a readable book and it is one which should be a useful companion to an honours student in his final year, when the threads of earlier study are being gathered together. The treatment is along modern lines and, in particular, the author has made ample and satisfactory use of Werner's theory of complex compounds. The student who has the impression that inorganic chemistry is a subject disposed of at an early part of a course of study will be surprised to find how much he did not know and the teacher will also be grateful to the author for such a handy compendium, with references to the original recent literature. This is a book which may be cordially recommended to advanced students and to those who wish to revise their knowledge of inorganic chemistry.—*Transactions of the Faraday Society.*

From the viewpoint of the advanced student of inorganic chemistry there has always been a gap in the literature of the subject between the conventional text-books on the one hand and the encyclopædic, dictionary-type publications and the original literature on the other. With a view to bridging over this gap, Dr Ephraim, who is Professor of Chemistry in the University of Berne, prepared the present work. Mr Thorne has made his translation from the third German edition, and much additional matter furnished by Dr Ephraim has been included. Advanced students in Universities and technical colleges, in addition to chemists who have completed their training, will be grateful to Mr Thorne for his efforts in producing an English edition of Dr Ephraim's work.—*Chemical Trade Journal.*

There is no doubt that a student who has already reached the standard of a pass degree, and wishes to find a suitable book to read in preparation for an honours degree, will find Prof. Ephraim's text-book extremely useful and stimulating.—*Nature.*

The book will undoubtedly be of the greatest use to advanced students. The very large amount of material contained in the book makes it a useful work of reference. Text-books on inorganic chemistry of the size of the present work are frequently tedious to read, by reason of the many repetitions and the wearisome and laboured descriptions of multitudes of compounds. Such a fault does not occur in Professor Ephraim's book. The translator has done his work exceedingly well. The book is clearly indexed and printed, and in every respect it is an excellent production, which can be recommended without reservation to advanced students of chemistry.—*Journal of the Institute of Metals.*

As a book of general interest to the chemist, the work can be recommended for the clear presentation and logical application of the theory and generalisation of inorganic chemistry. Slight reference has been made here to the text devoted to descriptive material and the properties of compounds. This is quite extensive, as the size of the book indicates. The work meets the need for variation in the method of presentation, brought about by recent contributions to our general knowledge of the subject.—*Canadian Chemistry and Metallurgy.*